Chemistry of *N*-Sulfonyl-Substituted Thiiranimines

Gerrit L'abbé,* Jean-Paul Dekerk, Catherina Martens, and Suzanne Toppet

Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3030 Heverlee, Belgium

Received June 9, 1980

A synthetic route to the title compounds involving the reactions of sulfonyl isothiocyanates with diphenyldiazomethane is described. The three-membered rings thus obtained (**3a,b**) were fully characterized by spectral methods, particularly IR and ^{13}C NMR. An X-ray analysis revealed the presence of a weak C^2–S bond which is also cleaved by thermolysis and reactions with nucleophiles, as well as in ring transformations with enamines, ynamines, aldehydes, and isonitriles. The cycloaddition reactions can occur by three different pathways (**3** being a tridentate reagent), depending on the nature of the reaction partner.

Unsaturated three-membered heterocycles of type **1**

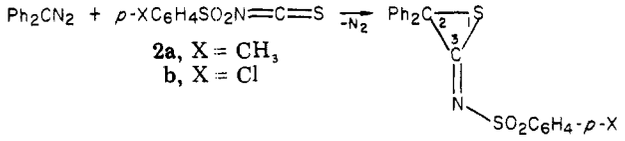
1, X, Y, Z = R_2C, O, S, NR

possess a high energy content which precludes their isolation in many synthetic approaches. The unusual reactivity associated with their ring strain has spurred considerable activity in this field, and a large amount of information has accumulated during the last two decades.[1] Representatives of many classes can now be prepared in the pure state, but several other class members still remain as elusive intermediates in spite of much effort toward their isolation or detection by spectral methods. Examples of the latter are the three-membered-ring thiones, oxiranimines, thiaziridinimines,[1] and even the title compounds before we initiated our research in this field.[2]

In principle, thiiranimines should be accessible from the reactions of diazoalkanes with isothiocyanates after loss of nitrogen. All the publications on this subject, however, deal with diazomethane or monosubstituted diazoalkanes which lead to the aromatic 1,2,3-thiadiazoles.[3] We give here a full account of our work on the synthesis, spectral characterization, and chemical behavior of the substituted thiiranimines.

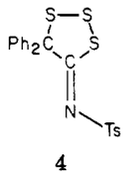
Synthesis

The reactions of diphenyldiazomethane with arylsulfonyl isothiocyanates **2a,b** proceed readily at 0 °C with evolution



2a, X = CH_3
b, X = Cl

3a, X = CH_3
b, X = Cl



4

Table I. IR Data of 3a

solvent (dielectric const)	ν_1, cm^{-1}	ν_2, cm^{-1}	$\Delta\nu$, cm^{-1}	R^a	ν_0, cm^{-1} (calcd)
CCl_4 (2.2)	1700	1634	66	0.68	1673
CCl_2=CCl_2 (2.3)	1700	1630	70	0.85	1667
Et_2O (4.3)	1698	1629	69	0.90	1664
$CHCl_3$ (4.7)	1704	1630	74	1.10	1665
m-$C_6H_4Cl_2$ (5.0)	1702	1628	74	1.0	1665
CH_3CN (37.5)	1706	1623	83	1.8	1654
Me_2SO (48.9)		1650			1650
KBr disk	1710	1630	80	1.6	1660

[a] The *R* values are calculated from the ratio of intensities (I_2/I_1) and are only approximate.

of nitrogen. The products **3a,b** were isolated in 67–70% yield simply by cooling the solutions to −30 °C. In the case of **2a**, a small amount (ca. 1%) of the trithiolane **4** was also obtained from the residue by column chromatography.

From the mild reaction conditions it is evident that the formation of **3a,b** is not the result of a carbene addition onto the isothiocyanates; instead, a 1,3-dipolar cycloaddition occurs to yield unstable 1,2,3-thiadiazolinimines which subsequently decompose into the thiiranimines **3a,b**.

Spectral Characterization

Three-membered heterocycles with an exocyclic imine function exhibit a diagnostic C=N stretching vibration at very high frequency in the IR spectra, i.e., at 1780–1810 cm^{-1} for aziridinimines and diaziridinimines.[4] The C=N frequency, however, is shifted downward to 1750 cm^{-1} when a tosyl substituent is attached at the exocyclic nitrogen atom.[5]

In our case, the solid-state IR spectra of **3a,b** manifest a medium band at 1710 cm^{-1} (ν_1) and a strong broad absorption at 1630 cm^{-1} (ν_2). In order to get more insight into this phenomenon, we recorded the spectra of **3a** in several solvents, and the results are summarized in Table I. The distance between the two absorptions ν_1 and ν_2 ($\Delta\nu$) increases with the polarity of the solvent, while at the same time the relative intensity of the lower frequency band increases. This indicates the presence of Fermi resonance between the C=N stretch and an overtone or combination band.[6] The position of the fundamental vibration ν_0 can be calculated from the observed absorptions[6] and is given in Table I; it shifts downward as the polarity of the solvent increases. In Me_2SO as solvent, no Fermi resonance occurs, and the C=N stretching absorption is found at 1650 cm^{-1}.

(1) Review: L'abbé, G. *Angew. Chem.* **1980**, *92*, 277; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 276.

(2) For preliminary reports on this topic, see: L'abbé, G.; Dekerk, J.-P.; Declercq, J.-P.; Germain, G.; Van Meerssche, M. *Angew. Chem.* **1978**, *90*, 207; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 195; *Tetrahedron Lett.* **1979**, 1819, 3213.

(3) Eistert, B.; Regitz, M.; Heck, G.; Schwall, H. In "Methoden der organischen Chemie (Houben-Weyl)" Georg Thieme Verlag: Stuttgart, 1968; Vol. X/4, pp 785–786. Goerdeler, J.; Gnad, G. *Chem. Ber.* **1966**, *99*, 1618. Hoff, S.; Blok, A. P. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 317. Regitz, M.; Weber, B.; Heydt, A. *Liebigs Ann. Chem.* **1980**, 305.

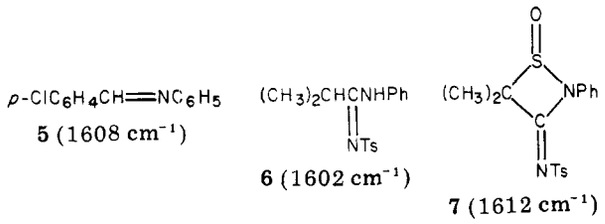
(4) Quast, H.; Schmitt, E. *Angew. Chem.* **1970**, *82*, 395; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 381; *Chem. Ber.* **1970**, *103*, 1234.

(5) L'abbé, G.; Verbruggen, A. *Tetrahedron Lett.* **1979**, 49.

(6) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. In "Introduction to Infrared and Raman Spectroscopy", 2nd ed.; Academic Press: New York, 1975; pp 28–30.

0022-3263/80/1945-4366$01.00/0

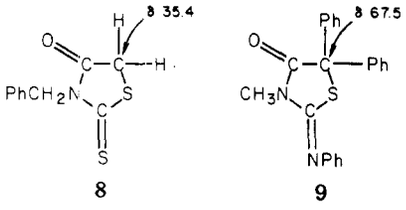
Since the model compounds **5–7** do not show this splitting



behavior (KBr disks), we tentatively attribute the Fermi resonance to an interaction of the fundamental C=N vibration with an overtone or combination band of the ring vibration.

The ^{13}C NMR spectra of the thiiranimines are also informative. Indeed, it is known that three-membered rings manifest a significant upfield shift compared to larger rings. For instance, thiirane absorbs at δ 18.7 compared to δ 32.5 for thiolane.[7] The same phenomenon is observed in our spectra ($CDCl_3$); namely, the ring carbon atoms of **3a,b** resonate at δ 47 (C^2) and 171 (C^3) whereas those of the trithiolane **4** are found at δ 83.5 and 189.4.

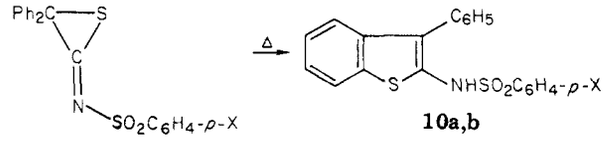
In order to evaluate the influence of the two phenyl substituents on the absorption position of the ring carbon atom, we have compared the NMR spectra (in $CDCl_3$) of two model compounds, **8** and **9**. A substituent effect of 32 ppm is noticed for the C_5 signal which is comparable with $\Delta\delta$ = 28 ppm for the corresponding chemical shift difference between thiirane and **3a,b**.



8 **9**

Thermolysis and Ring-Opening Reactions

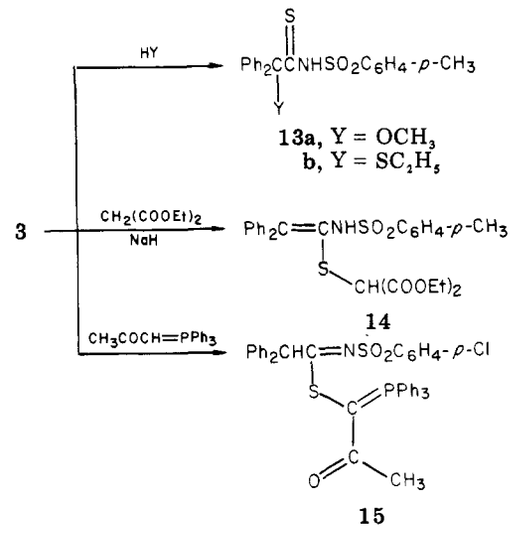
An X-ray diffraction analysis of **3a** reveals the presence of an unusually large C^2–S distance of 1.94 Å, compared with the normal C–S bond length of 1.84 Å in compound **4**.[2] In addition, the two other bonds C^2–C^3 (1.47 Å) and C^3–S (1.70 Å) are shorter than normally expected for the sum of the covalent radii, a situation also observed for aziridinimines[8] and diaziridinimines.[9] The weakness of the C^2–S bond is also reflected in the thermal lability and high reactivity of **3a,b**. Thus, **3a** and **3b** are stable in the crystalline state at room temperature for a long period, but in chloroform solution slow isomerization occurs to give the benzothiophenes **10a,b**. At reflux temperature, de-



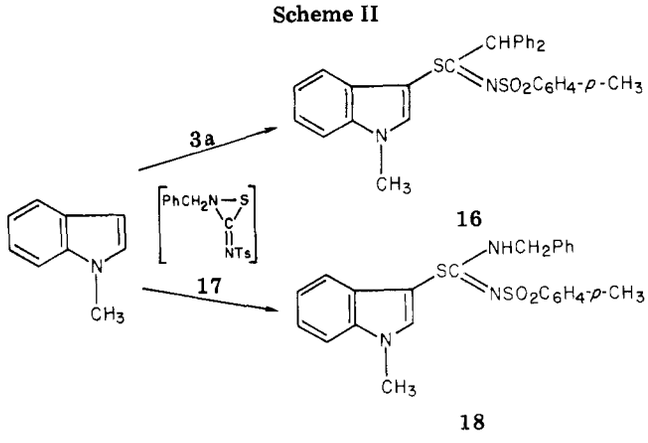
3a,b **10a,b**

composition is complete within 2 h. The benzothiophenes **10a,b** are also formed as side products during the synthesis of **3a,b** if the reactions are carried out, or worked up, without cooling. Our success in the synthesis and isolation

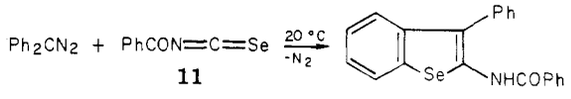
Scheme I



Scheme II



of **3** thus comes from the favorable reaction conditions (0 °C) which were not met in our attempts to prepare the selenium analogues. Indeed, benzoyl isoselenocyanate (**11**)



12

and diphenyldiazomethane do not react below room temperature, when the reaction is very slow (12 h), and yield directly the benzoselenophene **12**. Furthermore, our attempts to prepare a more stable thiiranimine by using dimesityldiazomethane or di-*tert*-butyldiazomethane instead of diphenyldiazomethane failed, since no reaction was observed with tosylisothiocyanate.

In principle, three electrophilic positions (C^2, C^3, and S) are available in **3** for attack by nucleophiles, but only two pathways have been found which correspond to C^2–S bond cleavage. Thus, methanolysis of **3a** yields the thioamide **13a**, and reaction of **3a** with diethyl malonate gives **14**. The difference in reactivity between heteronucleophiles and C-nucleophiles is further exemplified by the reactions of **3** (Scheme I) with ethanethiol and acetylmethylenetriphenylphosphorane, giving, respectively, **13b** and the new functionalized ylide **15**.

Thiiranimine **3a** also reacts as an electrophilic species with *N*-methylindole at 0 °C to give derivative **16** (Scheme II), a reaction which we have also encountered with the three-membered ring **17**. The latter was prepared in situ by thermolysis of 4-benzyl-5-(tosylimino)-1,2,3,4-thiatriazoline at 60 °C.[10] The structure of product **18** was verified

(7) Levy, G. C.; Nelson, G. L. In "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972; p 52.
(8) Quast, H.; Schäfer, P.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1980**, *113*, 1921.
(9) Peters, K.; von Schnering, G. *Chem. Ber.* **1976**, *109*, 1384.

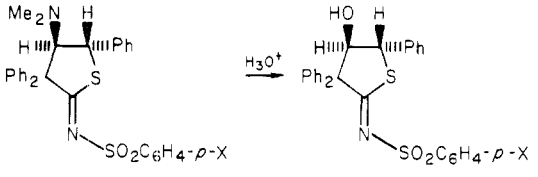
by comparison with an authentic sample prepared from *N*-methylindole and *N*-benzyl-*N'*-tosylthiourea in the presence of iodine–potassium iodide,[11] thus establishing the position of attachment of the sulfur atom in the indole ring.

From the results outlined above, it is evident that **3a** and **3b** behave as ambident electrophilic systems with the C^2 and S atoms as centers for nucleophilic attack.

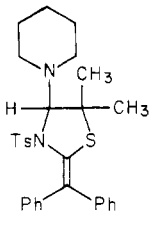
Cycloaddition Reactions

The behavior of **1** (Z = NR) in cycloaddition reactions is well documented for the elusive thiaziridinimines (e.g., **17**);[1] for stable derivatives our knowledge is limited to only two reports on diaziridinimines.[12] Their reactions with phenyl isocyanate and dimethyl acetylenedicarboxylate yield cycloadducts which result from initial nucleophilic attack of the exocyclic imine function on the electrophilic center of the reaction partner. In our cases, the C^2–S bond of **3a,b** is cleaved in cycloaddition reactions, and three different pathways are found, involving participation of either the C^2 and S, the N and S, or the C^2 and N atoms, depending on the nature of the coreagent as shown below.

trans-β-(Dimethylamino)styrene combines with **3a,b** at 0 °C to give the thiolanimines **19a,b** which hydrolyze readily into **20** under the influence of hydrochloric acid.



19a,b **20**

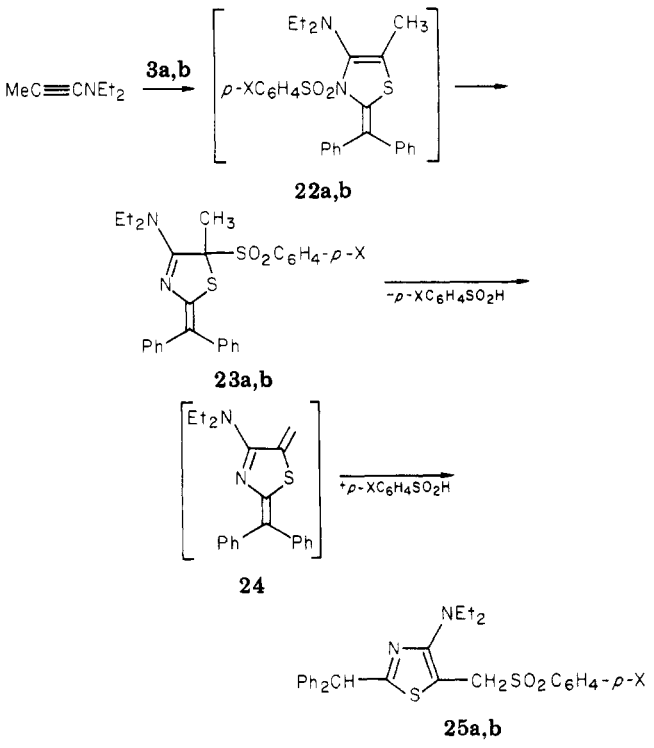


21

In contrast, 1-piperidinoisobutene yields a cycloadduct with a different ring skeleton, **21**, thus pointing to a different mode of addition. Another enamine, namely, 1-(dimethylamino)isobutene, did not react with **3** under similar conditions; neither were additions observed with the electron-rich double bonds of vinyl azides.

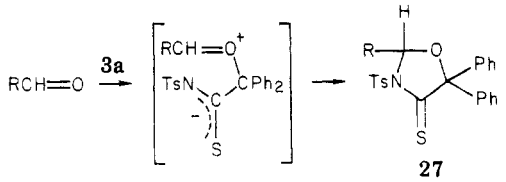
(Diethylamino)propyne is a case of special interest. At 0 °C, it interacts with the N and S atoms of **3a,b** to yield unstable adducts **22a,b** (Scheme III) which undergo a spontaneous sulfonyl migration from N^3 to C^5. The resulting products, **23a,b**, can be isolated and characterized as such, but they further isomerize in solution at room temperature to give the aromatic thiazole derivatives **25a,b**. The mechanism of this reaction probably involves a sequence of elimination and readdition of arylsulfinic acid. The elimination step is analogous to the well-known thermal elimination of sulfenic acids from sulfoxides to produce olefins.[13] Support for this mechanism in our

Scheme III



22a,b **23a,b** **24** **25a,b**

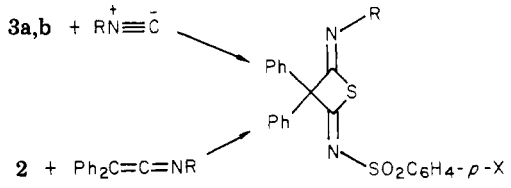
Scheme IV[a]



26 **27**

[a] a, R = CH_3; b, R = C_6H_5; c, R = *m*-$NO_2C_6H_4$; d, R = $CH{=}CH_2$.

Scheme V



28a, R = *p*-$CH_3OC_6H_4$; X = CH_3
b, R = $(CH_3)_3C$; X = Cl

reactions comes from the mass spectra of **23a,b** which exhibit significant fragment ion peaks at *m/e* 334 attributable to **24**.

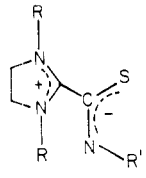
A third series of reactions with **3a** are those of aldehydes which furnish C^2–N addition products **27** (Scheme IV). The yields obtained in these cycloadditions increase as the electron density of the aldehyde increases: R = CH_3 (68%) > C_6H_5 (17%) > *m*-$NO_2C_6H_4$ (12%). This points to a nucleophilic nature for the aldehyde, reacting via intermediate **26**.

Finally, we have also considered, with success, the possibility of achieving [3 + 1] cycloaddition reactions of **3a,b** with isonitriles. The iminothietanes **28a,b** thus formed (Scheme V) constitute an unexplored class of re-

(10) L'abbé, G.; Van Loock, E.; Albert, R.; Toppet, S.; Verhelst, G.; Smets, G. *J. Am. Chem. Soc.* **1974**, *96*, 3973.
(11) Harris, R. L. N. *Tetrahedron Lett.* **1969**, 4465.
(12) Quast, H.; Spiegel, E. *Angew. Chem.* **1977**, *89*, 112; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 109. Quast, H.; Ross, K.-H.; Spiegel, E.; Peters, K.; von Schnering, H. G. *Angew. Chem.* **1977**, *89*, 202; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 177.
(13) See, for instance: Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887 and references cited therein.

active heterocycles, of which only a few examples have been reported recently.[14] An alternative approach to this ring system involves a [2 + 2] cycloaddition of **2** with ketenimines. This reaction has been applied to the synthesis of **28a** in 54% yield and is the most convenient of the two methods for synthetic purposes.

It is interesting to note that thioketones, nitriles, dimethyl acetylenedicarboxylate, isocyanates, isothiocyanates, and ketenes were unreactive toward **3a,b**. This contrasts sharply with the chemical behavior of the known inner salts of type **29** which only react with electrophilic



29

partners in cycloaddition reactions.[15] This is a typical situation of "umpolung"[16] of reactivity in going from the closed-ring to the open-chain dipolar species.

The factors which govern the three different modes of cycloaddition reactions of **3** have not been elucidated. The structures of our cycloadducts, on the contrary, were unambiguously assigned on the basis of spectral and X-ray analyses. Since their important features were discussed in the preliminary reports,[2] we defer the data to the Experimental Section.

Experimental Section

Synthesis of 3a,b. To an ice-cooled solution of diphenyldiazomethane (2×10^{-2} mol) in dry ether (30 mL) was added dropwise during 1 h an equimolar amount of tosyl isothiocyanate in 30 mL of ether. After nitrogen evolution had ceased, the solution was cooled to −30 °C, yielding **3a** (67%). The filtrate was evaporated and the residue subjected to column chromatography on silica gel with benzene–ethyl acetate (95:5) as the eluent. This furnished **4** in 1% yield.

Compound **3a** was recrystallized from ether: mp 86 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 3 H, CH_3), 7.2–7.9 (m, 14 aromatic H); ^{13}C NMR ($CDCl_3$) δ 21.8 (CH_3), 46.5 (C^2), 128–131 (5 aromatic CH), 136.0, 137.3, and 145.3 (aromatic C quat), 170.1 (C^3); mass spectrum, *m/e* (relative intensity) 379 (5, $M^{+\cdot}$), 223 (3, $M^{+\cdot}$ − TsH), 192 (100, Ph_2C^+CN). Anal. Calcd for M^+: *m/e* 379.0701. Found: *m/e* 379.0686.

Compound **3b** was similarly prepared in 70% yield and recrystallized from ether: mp 78–82 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.3–7.9 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 47.3 (C^2), 128.5–130 (5 aromatic CH), 136.9, 137.4, 140.7 (aromatic C quat), 171.4 (C^3); mass spectrum, *m/e* (relative intensity) 401 and 399 (7 and 19, $M^{+\cdot}$), 224 (100, $M^{+\cdot} - ClC_6H_4SO_2$), 223 (50, $M^{+\cdot} - ClC_6H_4SO_2H$), 192 (72, Ph_2C^+CN). Anal. Calcd for $C_{20}H_{14}ClNO_2S_2$ (mol wt 400): C, 60.07; H, 3.53. Found: C, 59.84; H, 3.61.

Compound **4** was isolated as yellow needles: mp 186–187 °C; IR (KR) 1525 cm^{-1} (s br, C=NTs); ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 21.7 (CH_3), 83.3 (Ph_2C), 127.8–130 (aromatic CH), 136.0, 137.1, and 145.1 (aromatic C quat), 189.4 (C=N); mass spectrum, *m/e* (relative intensity) 379 (13, $M^{+\cdot}$ − 2 S), 347 (4, $M^{+\cdot}$ − 3 S), 224 (40, $M^{+\cdot}$ − 2 S − Ts), 192 (100, Ph_2C^+CN). Anal. Calcd for $C_{21}H_{17}NO_2S_4$ (mol wt 444): C, 56.88; H, 3.86; N, 3.16; S, 28.91. Found: C, 56.66; H, 3.90; N, 3.15; S, 28.98.

Thermolysis of 3a,b. Compounds **3a,b** (10^{-3} mol) were heated in 20 mL of CCl_4 at reflux temperature for 4 h. After partial removal of the solvent, the solutions were cooled to −30 °C, yielding **10a,b**.

Compound **10a** was obtained in quantitative yield: mp 55–56 °C (ether); IR (KBr) 3240 cm^{-1} (NH); ^{1}H NMR (Me_2SO-d_6) δ 2.42 (s, 3 H, CH_3), 10.55 (s, NH); ^{13}C NMR ($CDCl_3$) δ 21.6 (CH_3), 122.6–144.8 (14 different aromatic C signals); mass spectrum, *m/e* (relative intensity) 379 (52, $M^{+\cdot}$), 224 (100, $M^{+\cdot}$ − Ts), 192 (33, $M^{+\cdot}$ − Ts − S). Anal. Calcd for $C_{21}H_{17}NO_2S_2$ (mol wt 379.5): C, 66.46; H, 4.52. Found: C, 66.59; H, 4.35.

Compound **10b** was obtained in 75% yield: mp 168–170 °C (CCl_4); IR (KBr) 3250 cm^{-1} (NH); ^{1}H NMR (Me_2SO-d_6) δ 7.08–7.88 (m, aromatic H), 10.60 (s, NH); ^{13}C NMR (Me_2SO-d_6) δ 122.7–138.7 (16 different aromatic C signals); mass spectrum, *m/e* (relative intensity) 401 and 399 (12 and 27, $M^{+\cdot}$), 224 (100, $M^{+\cdot}$ − $ClC_6H_4SO_2$). Anal. Calcd for $C_{20}H_{14}ClNO_2S_2$ (mol wt 400): C, 60.07; H, 3.53. Found: C, 59.86; H, 3.43.

Reaction of Diphenyldiazomethane with Benzoyl Isoselenocyanate. Benzoyl isoselenocyanate was prepared in situ by adding benzoyl chloride (0.01 mol) to a solution of potassium selenocyanate (1.45 g) in 20 mL of acetone as reported.[17] Then diphenyldiazomethane (0.01 mol) was added dropwise and the reaction mixture stirred for 12 h. After removal of the precipitate (containing KCl and polymers), the filtrate was evaporated and the residue triturated with ether to give a yellow product, **12**: 27% yield; mp 182 °C (ether–chloroform); IR (KBr) 3400 (NH), 1660 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 7.2–8.0 (m, 14 aromatic H), 8.8 (br, NH); ^{13}C NMR (Me_2SO-d_6) δ 123–139 (16 different aromatic C signals), 165.6 (C=O); mass spectrum, *m/e* (relative intensity) 377 and 375 (28 and 15, $M^{+\cdot}$), 105 (100, $PhCO^+$), 77 (34, Ph^+). Anal. Calcd for $C_{21}H_{15}NOSe$ (mol wt 377): C, 66.83; H, 4.01. Found: C, 66.71; H, 4.06.

Methanolysis of 3a. A solution of **3a** in methanol (100 mg in 5 mL) was refluxed for 1 h and then cooled to room temperature, giving **13a** as yellow needles in quantitative yield: mp 128–130 °C (MeOH); IR (KBr) 3220 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3 H, CH_3), 3.00 (s, 3 H, CH_3O), 10.7 (br, NH); ^{13}C NMR ($CDCl_3$) δ 21.7 (CH_3), 53.5 (CH_3O), 93.6 (Ph_2CO), 128.1–130.2 (aromatic CH), 133.1, 138.4, and 145.5 (aromatic C quat), 204.6 (C=S); mass spectrum, *m/e* (relative intensity) 379 (16, $M^{+\cdot}$ − MeOH), 197 (100, Ph_2C^+OMe), 192 (67, Ph_2C^+CN). Anal. Calcd for $C_{22}H_{21}NO_3S_2$ (mol wt 412): C, 64.20; H, 5.14; N, 3.40. Found: C, 64.13; H, 5.09; N, 3.38.

Reaction of 3a with Ethanethiol. A solution of **3a** in ethanethiol (400 mg in 5 mL) was refluxed for 1 h. The excess thiol was distilled off and the residue triturated with dry ether to give **13b** in quantitative yield: mp 139–140 °C (MeOH); IR (KBr) 3210 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ 1.1 (t, 3 H, CH_3), 2.2 (q, 2 H, CH_2), 2.4 (s, 3 H, CH_3), 7.1–7.8 (m, 14 aromatic H), 10.2 (br, NH); ^{13}C NMR ($CDCl_3$) δ 13.3 (CH_3), 21.9 (CH_3), 26.6 (CH_2), 75.2 (Ph_2C), 128.1–129.6 (aromatic CH), 133.8, 141.2, and 145.7 (aromatic C quat), 201.8 (C=S); mass spectrum, *m/e* (relative intensity) 441 (4, $M^{+\cdot}$), 348 (4, Ph_2C=C=$NHTs^+$), 227 (8, Ph_2CSEt^+), 192 (100, Ph_2C^+CN), 165 (40, $C_6H_5C_7H_4^+$). Anal. Calcd for $C_{23}H_{23}NO_2S_3$ (mol wt 441): C, 62.55; H, 5.25. Found: C, 62.50; H, 5.24.

Reaction of 3a with Diethyl Malonate. Diethyl malonate (670 mg) was allowed to react with an equimolar amount of NaH (100 mg) in 5 mL of THF at room temperature for 10 min. The solution was cooled to 0 °C, and an equimolar amount of **3a** (1.56 g) in 5 mL of ether was added. After a reaction time of 3 h at 0 °C, the mixture was poured into water and then extracted with chloroform. The extracts were dried over Na_2SO_4 and evaporated to give **14** which was crystallized from methanol in 27% yield: mp 159–160 °C; IR (KBr) 3220 (s, NH), 1715 cm^{-1} (s, C=O); ^{1}H NMR ($CDCl_3$) δ 1.23 (t, 6 H, 2 CH_3), 2.42 (s, 3 H, CH_3), 4.15 (q, 4 H, 2 CH_2), 4.65 (s, 1 H, CH), 6.7 (s, NH), 6.8–7.8 (m, 14 aromatic H); ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 21.8 (CH_3), 52.0 (CHS), 62.5 (CH_2), 128.3–130 (aromatic CH), 125.4 (Ph_2C=C), 136.5, 139.4,

(14) Dondoni, A.; Battaglia, A.; Giorgianni, P.; Gilli, G.; Sacerdoti, M. *J. Chem. Soc., Chem. Commun.*, **1977**, 43. Visser, R. G.; Baaij, J. P. B.; Brouwer, A. C.; Bos, H. J. T. *Tetrahedron Lett.* **1977**, 4343. Bestmann, H. J. *Angew. Chem.* **1977**, *89*, 370; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 358. L'abbé, G.; Huybrechts, L.; Declercq, J.-P.; Germain, G.; Van Meerssche, M. *J. Chem. Soc., Chem. Commun.* **1979**, 160.

(15) Winberg, H. E.; Coffman, D. D. *J. Am. Chem. Soc.* **1965**, *87*, 2776. Regitz, M.; Schössler, W.; Weber, B.; Liedhegener, A. *Justus Liebigs Ann. Chem.* **1971**, *748*, 1. Schössler, W.; Regitz, M. *Chem. Ber.* **1974**, *107*, 1931.

(16) For reviews on the concept of "umpolung" see: Seebach, D. *Angew. Chem.* **1969**, *81*, 690; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 639. Seebach, D.; Kolb, M. *Chem. Ind. (London)* **1974**, 687. Seebach, D.; Enders, D. *Angew. Chem.* **1975**, *87*, 1; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 1.

(17) Douglass, I. B. *J. Am. Chem. Soc.* **1937**, *59*, 740.

140.1, and 144.2 (aromatic C quat), 144.4 (Ph_2C=C), 166.5 (C=O); mass spectrum, *m/e* (relative intensity) 539 (2, $M^{+\cdot}$), 347 (5, Ph_2C=C=$NTs^{+\cdot}$), 192 (100, Ph_2C^+CN), 165 (35, $C_6H_5C_7H_4^+$). Anal. Calcd for $C_{28}H_{29}NO_6S_2$ (mol wt 539): C, 62.38; H, 5.42. Found: C, 62.26; H, 5.38.

Reaction of 3b with Acetylmethylenetriphenylphosphorane. To an ice-cooled solution of **3b** (10^{-3} mol) in chloroform was added dropwise an equimolar amount of the ylide in 10 mL of chloroform. The solution was allowed to react at 0 °C for 5 h. After removal of the solvent, the residual oil was crystallized from methanol, yielding **15** in 28% yield: mp 176–178 °C (MeOH); IR (KBr) 1540 cm^{-1} (C=NSO_2); ^1H NMR ($CDCl_3$) δ 1.95 (s, 3 H, CH_3), 6.46 (s, 1 H, CH), 6.5–7.8 (m, 29 aromatic H); ^{13}C NMR ($CDCl_3$) δ 25.7 (d, CH_3CO, $^3J_{CP}$ = 4.8 Hz), 50.3 (d, C=P, $^1J_{CP}$ = 115 Hz), 55.9 (Ph_2CH), 123.6–139.5 (aromatic C signals), 194.5 (C=N), 197.5 (C=O). Anal. Calcd for $C_{41}H_{33}ClNO_3PS_2$ (mol wt 718): C, 68.56; H, 4.63. Found: C, 68.12; H, 4.54.

Reaction of 3a with *N*-Methylindole. *N*-Methylindole (350 mg) in 5 mL of CCl_4 was added dropwise to an ice-cooled solution of **3a** (758 mg) in 5 mL of dry CCl_4. After a reaction time of 3 h at 0 °C, the solution was kept at room temperature for another 12 h. The solvent was then removed in vacuo, and the residue was triturated with ether to give **16**. Side products from this reaction were **10a** and polymers. Compound **16** was obtained in 39% yield after recrystallization from methanol: mp 182–183 °C; ^1H NMR ($CDCl_3$) δ 2.36 (s, 3 H, CH_3), 3.60 (s, 3 H, CH_3N), 5.3 (br, 1 H, not exchangeable with D_2O), 6.52 (s, 1 H, indole C^2 H), 6.7–7.7 (m, 16 aromatic H), 7.6 (d, 2 aromatic H); ^{13}C NMR ($CDCl_3$) δ 21.5 (CH_3), 33.1 (CH_3N), 58.4 (Ph_2CH), 96.9 (diagnostic for indole C^3), 110.1–136.4 (aromatic CH), 129.5, 137.3, 138.4, 139.6, and 143.3 (aromatic C quat), 189.7 (C=N); mass spectrum, *m/e* (relative intensity) 510 (7, $M^{+\cdot}$), 347 (8, Ph_2C=C=$NTs^{+\cdot}$), 192 (100, Ph_2C^+CN), 163 (53, $M^{+\cdot} - Ph_2C$=C=NTs), 162 (71), 91 (18, $C_7H_7^+$). Anal. Calcd for $C_{30}H_{26}N_2O_2S_2$ (mol wt 510): C, 70.56; H, 5.13; N, 5.48. Found: C, 70.42; H, 5.13; N, 5.38.

Reaction of 17 with *N*-Methylindole. Equimolar amounts (0.01 mol) of 4-benzyl-5-(tosylimino)-1,2,3,4-thiatriazoline and *N*-methylindole were heated in 25 mL of CCl_4 at 60 °C until nitrogen evolution ceased (2 h) and then at 80 °C for another 1 h. The solution was cooled to room temperature, and the white precipitate **18** was filtered off, washed with CCl_4, and recrystallized from methanol: yield 80%; mp 167–169 °C; IR (KBr) 3300 (NH), 1530 cm^{-1} (br s, C=N); ^1H NMR ($CDCl_3$) δ 2.42 (s, 3 H, CH_3), 3.78 (s, 3 H, CH_3N), 4.35 (d, 2 H, CH_2N), 5.85 (br t, NH), 6.7–7.45 (m, 12 aromatic H), 7.85 (d, 2 aromatic H); ^{13}C NMR ($CDCl_3$) δ 21.6 (CH_3), 33.6 (CH_3N), 47.2 (CH_2), 94.7 (diagnostic for indole C^3), 110.7–129.4 and 138.1 (aromatic CH), 129.0, 136.9, 137.1, 140.3, and 142.6 (aromatic C quat), 165.3 (C=N); mass spectrum, *m/e* (relative intensity) 449 (<1, $M^{+\cdot}$), 162 (20), 163 (50, $M^{+\cdot} - PhCH_2N$=C=NTs), 162 (20), 155 (36, Ts^+), 148 (10), 131 (30), 91 (100, $C_7H_7^+$). Anal. Calcd for $C_{24}H_{23}N_3O_2S_2$ (mol wt 449): C, 64.11; H, 5.16; N, 9.35. Found: C, 64.01; H, 5.18; N, 9.33.

Compound **18** was independently synthesized as follows. A methanol solution of I_2 (1.26 g) and KI (0.84 g) was added dropwise during 30 min to a heated solution of *N*-methylindole (0.66 g) and *N*-benzyl-*N'*-tosylthiourea (1.60 g) in 25 mL of methanol. The reaction mixture was heated for another 5 h and then cooled to room temperature. Compound **18** crystallized out in 50% yield.

Cycloadditions of 3 with Enamines. To an ice-cooled solution of **3** (10^{-3} mol) in 10 mL of dry ether was added dropwise an equimolar amount of coreagent in 10 mL of ether. The mixture was allowed to react at 0 °C for several hours. Then, the solvent was removed in vacuo, and the residue was crystallized from CCl_4.

Compound **19a** was obtained in 70% yield: mp 179–181 °C (MeOH); IR (KBr) 1560 cm^{-1} (br s, C=N); ^1H NMR ($CDCl_3$) δ 1.98 (s, 6 H, NMe_2), 2.38 (s, 3 H), 4.65 and 4.75 (AB pattern, CHCH, J_{AB} = 10 Hz), 7.1–7.65 (m, 14 aromatic H); ^{13}C NMR ($CDCl_3$) δ 21.5 (CH_3), 44.0 (CH_3N), 51.4 (CHPh), 69.7 (CPh_2), 75.8 (CHN), 127.3–130.3 (aromatic CH), 136–143 (5 aromatic C quat), 191.5 (C=N); mass spectrum, *m/e* (relative intensity) 526 (1.5, $M^{+\cdot}$), 327 (25, $M^{+\cdot} - NMe_2 - Ts$), 147 (100, $PhCH$=$CHNMe_2^{+\cdot}$). Anal. Calcd for $C_{31}H_{30}N_2O_2S_2$ (mol wt 527): C, 70.69; H, 5.74. Found: C, 70.53; H, 5.76.

This compound (5×10^{-4} mol) was treated with 10 mL of a 2 N solution of hydrochloric acid in 20 mL of DMF at room temperature for 3 days. Then, the solvent was poured into ice–water, yielding **20** in 60% after recrystallization from CCl_4: mp 238–242 °C; IR (KBr) 3410 (OH), 1560 cm^{-1} (br s, C=N); ^1H NMR (Me_2SO-d_6) δ 2.4 (s, 3 H, CH_3), AMX pattern for CH_MOH_X-CH_APh with absorptions at 4.3 (d, 1 H, J_{AM} = 10 Hz), 5.15 (dd, 1 H, J_{AM} = 10 Hz, J_{MX} = 7 Hz), and 6.22 (d, OH, J_{MX} = 7 Hz), 7.0–7.8 (m, 19 aromatic H); ^{13}C NMR (Me_2SO-d_6) δ 21.0 (CH_3), 54.7 (CHPh), 67.6 (CPh_2), 80.4 (CHO), 126.9–129.9 (aromatic CH), 135.1, 136.1, 138, 141.6, and 144.4 (aromatic C quat), 190.3 (C=N); mass spectrum, *m/e* (relative intensity) 499 (18, $M^{+\cdot}$), 344 (10, $M^{+\cdot} - Ts$), 286 (21, $\overline{CHPhC(Ph)_2CHOH^{+\cdot}}$), 261 (12, *m/e* 286 – H_2O), 196 (5, Ph_2C=$CHOH^{+\cdot}$), 122 (5, $PhCH$=$S^{+\cdot}$), 91 (100, $C_7H_7^+$). Anal. Calcd for $C_{29}H_{25}NO_3S_2$ (mol wt 499): C, 69.71; H, 5.05. Found: C, 69.54; H, 5.12.

Compound **19b** was obtained in 70% yield: mp 183–185 °C (MeOH); IR (KBr) 1550 cm^{-1} (br s, C=N); ^1H NMR ($CDCl_3$) δ 1.94 (s, 6 H), 4.60 and 4.70 (AB pattern, CHCH, J_{AB} = 10 Hz), 7.2–7.6 (m, 19 aromatic H); ^{13}C NMR ($CDCl_3$) δ 44.0 (CH_3N), 51.7 (CHPh), 69.9 (CPh_2), 75.8 (CHN), 127.6–130.5 (aromatic CH), 136.6, 139, 139.3, 139.5, and 142.1 (aromatic C quat), 193.1 (C=N); mass spectrum, *m/e* (relative intensity) 546 (1.7, $M^{+\cdot}$), 147 (100, $PhCH$=$CHNMe_2^{+\cdot}$). Anal. Calcd for $C_{30}H_{27}ClN_2O_2S_2$ (mol wt 546): C, 65.86; H, 4.97. Found: C, 65.64; H, 4.84.

Compound **21** was obtained directly from the reaction mixture upon cooling: yield 75% (48% after recrystallization from ether–methanol): mp 162–164.5 °C; IR (KBr) 1595 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 1.44 (s, 6 H, 2 CH_3), 1.56 (br, 6 H, 3 CH_2), 2.36 (s, 3 H, CH_3), 2.6–3.4 (m, 4 H, 2 CH_2), 5.08 (s, 1 H, CH), 6.9–7.4 (m, 14 aromatic H); ^{13}C NMR ($CDCl_3$) δ 21.5 (CH_3), 24.5 and 32.5 ($(CH_3)_2C$), 24.7, 26.5, and 51.4 (pyrrolidino C atoms), 54.6 (ring C^5), 94.5 (ring C^4), 126.3–130.3 (aromatic CH and CPh_2), 137.2, 137.5, 140.8, 143.3, and 143.9 (aromatic C quat and ring C^2); mass spectrum, *m/e* (relative intensity) 518 (3, $M^{+\cdot}$), 289 (2, $M^{+\cdot} - TsH - Me_2C$=S), 192 (17, Ph_2C^+CN), 139 (100, $C_5H_{10}NCH$=$CMe_2^{+\cdot}$), 74 (2, Me_2C=$S^{+\cdot}$). Anal. Calcd for $C_{30}H_{34}N_2O_2S_2$ (mol wt 518): C, 69.46; H, 6.61; N, 5.40. Found: C, 69.27; H, 6.98; N, 5.01.

Cycloadditions of 3a,b with (Diethylamino)propyne. When equimolar amounts (10^{-3} mol) of **3a,b** and the ynamine were allowed to react in 15 mL of ether at 0 °C, the yellow products **23a,b** crystallized out from the solutions. After 1 day, the precipitates were filtered off and recrystallized.

Compound **23a** was isolated in 36% yield (not optimized): mp 117–120 °C (ether–petroleum ether); IR (KBr) 1550 cm^{-1} (br s, C=C); ^1H NMR ($CDCl_3$) δ 1.26 (t, 6 H), 2.22 (s, 3 H, ring CH_3), 2.36 (s, 3 H, CH_3), 3.30 (ABX_3, 1 H, J_{AB} = 14 Hz, J_{AX} = 7 Hz), 4.05 (ABX_3, 1 H, J_{AB} = 14 Hz, J_{BX} = 7 Hz), 6.9–7.9 (m, 14 aromatic H); ^{13}C NMR ($CDCl_3$) δ 13.5 (CH_3CH_2), 19.6 (ring CH_3), 21.7 (CH_3), 44.9 (NCH_2), 85.8 (ring C^5), 120.7 (Ph_2C=), 125.5–131.4 (8 aromatic CH), 131.6, 140.3, 142.3, and 145.8 (aromatic C quat), 143 (ring C^2), 161.6 (ring C^4); mass spectrum, *m/e* (relative intensity) 490 (0.6, $M^{+\cdot}$), 335 (100, $M^{+\cdot} - Ts$), 334 (49, $M^{+\cdot} - TsH$), 305 (16, $M^{+\cdot} - TsH - Et$). Anal. Calcd for $M^{+\cdot}$: *m/e* 490.1748. Found: *m/e* 490.1749.

In chloroform solution at room temperature, **23a** was quantitatively isomerized into **25a** within 10 days. When the reaction of **3a** with (diethylamino)propyne in $CDCl_3$ at 0 °C was monitored by NMR, **23a** was formed first and quantitatively; it then aromatized slowly into **25a**. This resulted in the disappearance of the ring CH_3 signal at δ 2.22 in favor of new absorptions at δ 4.50 (CH_2SO_2) and 5.68 (Ph_2CH methine proton). At the same time, the ABX_3 pattern of the *N*-methylene protons was transformed into a clear quartet at δ 2.79.

Compound **25a**: mp 119–121 °C (MeOH–H_2O); ^1H NMR ($CDCl_3$) δ 0.75 (t, 6 H), 2.39 (s, 3 H), 2.79 (q, 4 H), 4.50 (s, 2 H), 5.68 (s, 1 H), 7.1–7.7 (m, 14 aromatic H); ^{13}C NMR ($CDCl_3$) δ 13 (CH_3CH_2), 21.6 (CH_3), 48.4 (NCH_2), 54.6 (CH_2SO_2), 55.3 (Ph_2CH), 111.9 (ring C^5), 127.3–129.7 (aromatic CH), 135.4, 142, and 145 (aromatic C quat), 160.5 (ring C^4), 171.5 (ring C^2); mass spectrum, *m/e* (relative intensity) 490 (0.4, $M^{+\cdot}$), 335 (100, $M^{+\cdot} - Ts$). Anal. Calcd for $C_{28}H_{30}N_2O_2S_2$ (mol wt 491): C, 68.54; H, 6.16; N, 5.71. Found: C, 68.42; H, 6.10; N, 5.60.

Compound **23b** was isolated in 45% yield (not optimized): mp 127–129 °C (ether–acetone); IR (KBr) 1550 cm^{-1} (br s, C=C); ^1H NMR ($CDCl_3$) δ 1.24 (t, 6 H), 2.20 (s, 3 H), 3.30 (ABX_3, 1 H, J_{AB} = 14 Hz, J_{AX} = 7 Hz), 4.05 (ABX_3, 1 H, J_{AB} = 14 Hz, J_{BX} = 7

Hz), 6.9–8.0 (m, 14 aromatic H); ^{13}C NMR ($CDCl_3$) δ 13.5 (CH_3CH_2), 19.6 (ring CH_3), 45.1 (NCH_2), 86 (ring C^5), 121.5 (Ph_2C=), 126–133.1 (7 aromatic CH), 133.4, 140.4, 141.9, and 142.5 (aromatic C quat), 142.9 (ring C^2), 161.6 (ring C^4); mass spectrum, *m/e* (relative intensity) 334 (100, $M^{+\cdot} - ClC_6H_4SO_2H$), 306 (12, **24** – CH_2=CH_2), 305 (40, **24** – Et). Anal. Calcd for $C_{27}H_{27}ClN_2O_2S_2$ (mol wt 511): C, 63.45; H, 5.32; N, 5.48. Found: C, 63.30; H, 5.32; N, 5.53.

When the reaction of **3b** with (diethylamino)propyne was carried out in $CDCl_3$ at 0 °C and monitored by NMR, **25b** was formed quantitatively after 3 min; it then isomerized into **25b**: ^{1}H NMR ($CDCl_3$) δ 0.80 (t, 6 H), 2.86 (q, 4 H), 4.56 (s, 2 H), 5.68 (s, 1 H), 7.1–7.9 (m, 14 aromatic H); ^{13}C NMR ($CDCl_3$) δ 12.9 (CH_3CH_2), 48.6 (CH_3), 54.6 (CH_2SO_2), 55.4 (Ph_2CH), 111.2 (ring C^5), 127.7–130.6 (aromatic CH), 137, 141.2, and 142.0 (aromatic C quat), 160.2 (ring C^4), 172.4 (ring C^2).

Cycloadditions of 3a with Aldehydes. Equimolar amounts (10^{-3} mol) of **3a** and aldehyde were allowed to react in 5–10 mL of benzene at room temperature for 1 day. Then, the reaction mixture was subjected to column chromatography on silica gel with benzene as the eluent.

Compound **27a** was obtained in 68% yield after crystallization from chloroform–methanol: mp 166–168 °C; IR (KBr) 1265 cm^{-1} (s, > NC=S);[18] ^{1}H NMR ($CDCl_3$) δ 1.94 (d, 3 H, *J* = 5 Hz), 2.42 (s, 3 H), 5.82 (q, 1 H, *J* = 5 Hz), 7.2–7.8 (m, 14 aromatic H); ^{13}C NMR ($CDCl_3$) δ 21.7 (CH_3), 22.9 (ring CH_3), 92.1 (ring C^2), 97.4 (ring C^5), 127.6–129.4 (aromatic CH), 133.4, 137.8, 140.8, and 145.9 (aromatic C quat), 200.3 (C=S); mass spectrum, *m/e* (relative intensity) 423 (0.4, $M^{+\cdot}$), 210 (100, $\overline{OC(Ph)_2CHCH_3}^{+\cdot}$), 187 (45, Ph_2C=O^+H), 105 (29, $PhCO^+$), 86 (57, CH_3CHN=C=S^+). Anal. Calcd for $C_{23}H_{21}NO_3S_2$ (mol wt 424): C, 65.22; H, 5.00; N, 3.31. Found: C, 65.24; H, 5.14; N, 3.29.

Compound **27b** was obtained in 16.5% yield after crystallization from chloroform–methanol: mp 142–144 °C; IR (KBr) 1255 cm^{-1} (s, >NC=S); ^{1}H NMR ($CDCl_3$) δ 6.45 (s, 1 H), 2.38 (s, 3 H), 7.04–7.60 (m, 19 aromatic H); ^{13}C NMR ($CDCl_3$) δ 21.7 (CH_3), 94.3 (ring C^2), 98 (ring C^5), 127.8–130.5 (aromatic CH), 134.1, 136.5, 138.1, 140.4, and 145.8 (aromatic C quat), 200.2 (C=S); mass spectrum, *m/e* (relative intensity) 485 (0.4, $M^{+\cdot}$), 272 (95, $\overline{OC(Ph)_2CHPh}^{+\cdot}$), 192 (100, Ph_2C^+CN), 182 (8, $Ph_2CO^{+\cdot}$), 148 (72, $PhCHN$=C=S^+). Anal. Calcd for $C_{28}H_{23}NO_3S_2$ (mol wt 486): C, 69.25; H, 4.77; N, 2.88. Found: C, 69.08; H, 4.72; N, 2.78.

Compound **27c** was obtained in 12% yield: mp 193–195 °C (MeOH); IR (KBr) 1260 cm^{-1} (s, >NC=S); ^{1}H NMR ($CDCl_3$) δ 6.52 (s, 1 H), 2.40 (s, 3 H), 7.08–8.4 (m, 18 aromatic H); ^{13}C NMR ($CDCl_3$) δ 21.7 (CH_3), 92.9 (ring C^2), 98.4 (ring C^5), 123.7–134.6 (aromatic CH), 133.3, 137.2, 138.8, 139.8, 146.5, and 148.4 (aromatic C quat), 199.7 (C=S); mass spectrum, *m/e* (relative intensity) 530 (0.4, $M^{+\cdot}$), 317 (100, $\overline{OC(Ph)_2CHC_6H_4NO_2}^{+\cdot}$), 182 (12, $Ph_2CO^{+\cdot}$), 105 (52, $PhCO^+$). Anal. Calcd for $C_{28}H_{22}N_2O_5S_2$ (mol wt 531): C, 63.38; H, 4.18. Found: C, 63.14; H, 4.07.

Compound **27d** was obtained by reacting **3a** (0.5 g) with 10 mL of acrolein at room temperature for 12 h. After purification by column chromatography on silica gel with benzene as the eluent, **27d** was obtained in 35% yield: mp 153 °C ($CHCl_3$–MeOH); IR (KBr) 1255 cm^{-1} (s, >NC=S); ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 5.4–6.2 (m, 4 H), 7.2 (d, 2 aromatic H), 7.3 (s, 10 aromatic H), 7.8 (d, 2 aromatic H); ^{13}C NMR ($CDCl_3$) δ 21.9 (CH_3), 94.2 (ring C^2), 98.1 (ring C^5), 123 and 133.9 (CH_2=CH), 127.9–129.7 (aromatic CH), 133.1, 138.7, 140.9, and 146.1 (aromatic C quat), 199.7 (C=S); mass spectrum, *m/e* (relative intensity) 435 (0.3, $M^{+\cdot}$), 222 (100, $M^{+\cdot}$ – TsNCS), 192 (19, Ph_2C^+CN), 105 (40, $PhCO^+$). Anal. Calcd for $C_{24}H_{21}O_3NS_2$ (mol wt 436): C, 66.18; H, 4.86. Found: C, 65.94; H, 4.76.

Cycloadditions of 3a,b with Isonitriles. Equimolar amounts (10^{-3} mol) of **3a** and *p*-methoxyphenylisonitrile were allowed to react in 15 mL of dry ether at 0 °C for 1 day. After evaporation of the solvent, the reaction mixture was extracted with ether–hexane to yield **28a**. The residue was chromatographed on silica gel with hexane–ether (80:20) as the eluent, giving an additional crop of **28a**: total yield 33% after crystallization from ether–hexane; mp 135–136 °C; IR (KBr) 1710 (m, C=NAr), 1605 cm^{-1} (br s, C=NSO_2); ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3 H), 3.74 (s, 3 H, CH_3O), 6.8–7.8 (m, 18 aromatic H); ^{13}C NMR ($CDCl_3$) δ 21.7 (CH_3), 55.5 (CH_3O), 90 (CPh_2), 114.9–129.9 (aromatic CH), 136, 137.7, 140.3, 145.1, and 158 (aromatic C quat), 156 (C=N), 180.1 (C=NSO_2); mass spectrum, *m/e* (relative intensity) 512 (0.1, $M^{+\cdot}$), 347 (3, Ph_2C=C=$NTs^{+\cdot}$), 299 (14, Ph_2C=C=$NC_6H_4OCH_3^{+\cdot}$), 192 (100, Ph_2C^+CN), 165 (30, $CH_3OC_6H_4NCS^{+\cdot}$). Anal. Calcd for $C_{29}H_{24}N_2O_3S_2$ (mol wt 513): C, 67.94; H, 4.72; N, 5.46. Found: C, 68.10; H, 4.85; N, 5.45.

Compound **28a** was independently prepared by reacting tosyl isothiocyanate (6.4×10^{-3} mol) with an equimolar amount of *N*-(*p*-methoxyphenyl)diphenylketenimine (1.93 g) in 10 mL of CCl_4 at reflux temperature for 2 days. After removal of the solvent, the solid residue was crystallized from ether to give **28a** in 54% yield.

Compound **28b** was obtained by reacting **3b** (10^{-3} mol) with 2 equiv of *tert*-butylisonitrile in 5 mL of ether at 0 °C for 1 day. After column chromatography on silica gel with CCl_4–EtOAc (98:2) as the eluent, **28b** was obtained in 52% yield: mp 144–145 °C (ether–hexane); IR (KBr) 1725 (w, C=NBu) 1600–1590 cm^{-1} (br s, C=NSO_2); ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 9 H), 6.72–7.86 (m, 15 aromatic H); ^{13}C NMR ($CDCl_3$) δ 29.0 (CH_3), 58.7 (CMe_3), 91.9 (CPh_2), 127.4–129.8 (aromatic CH), 138, 138.2, and 140.7 (aromatic C quat), 146.7 (C=N), 184.3 (C=NSO_2); mass spectrum, *m/e* (relative intensity) 483 (0.4, $M^{+\cdot}$ + 1), 367 (53, Ph_2C=C=$NSO_2C_6H_4Cl^{+\cdot}$), 290 (60, PhC=C=$NSO_2C_6H_4Cl^+$), 275 (87, $Ph_2C(CN)C$≡N^+Bu), 249 (100, Ph_2C=C=$NBu^{+\cdot}$). Anal. Calcd for $C_{25}H_{23}ClN_2O_2S_2$ (mol wt 483): C, 62.16; H, 4.80; N, 5.80. Found: C, 61.70; H, 4.73; N, 5.88.

Registry No. 2a, 1424-52-8; **2b**, 1424-59-5; **3a**, 72047-57-5; **3b**, 72047-58-6; **4**, 65665-39-6; **10a**, 65665-37-4; **10b**, 74725-59-0; **11**, 14223-49-5; **12**, 74725-60-3; **13a**, 65665-38-5; **13b**, 74725-61-4; **14**, 74725-62-5; **15**, 74725-63-6; **16**, 74725-64-7; **17**, 74725-65-8; **18**, 74725-66-9; **19a**, 72047-45-1; **19b**, 72047-46-2; **20**, 74725-67-0; **21**, 74725-68-1; **23a**, 72047-59-7; **23b**, 72047-60-0; **25a**, 72047-64-4; **25b**, 72047-65-5; **27a**, 72047-61-1; **27b**, 72047-62-2; **27c**, 72047-63-3; **27d**, 74725-69-2; **28a**, 73317-89-2; **28b**, 73317-90-5; diphenyldiazomethane, 883-40-9; diethyl malonate, 105-53-3; acetylmethylenetriphenylphosphorane, 1439-36-7; *N*-benzyl-*N'*-tosylthiourea, 53016-96-9; *trans*-β-(dimethylamino)styrene, 14846-39-0; 1-methylindole, 603-76-9; (diethylamino)propyne, 4231-35-0; acetaldehyde, 75-07-0; benzaldehyde, 100-52-7; *m*-nitrobenzaldehyde, 99-61-6; 2-propenal, 107-02-8; *p*-methoxyphenylisonitrile, 10349-38-9; *N*-(*p*-methoxyphenyl)diphenylketenimine, 40012-82-6; *tert*-butylisonitrile, 7188-38-7.

(18) Jensen, K. A.; Nielsen, P. H. *Acta Chem. Scand.* **1966**, *20*, 597.