

Scheme 1.

Table 1. *N*-Aroyl and *N*-Acyl-S-thioaroylsulfenamides **2**

No.	Ar	R	Mp	Yield ^{a)}	Found (Calcd)/%		
			°C	%	C	H	N
2a	Ph	Ph	115	28	61.33 (61.51)	3.98 (4.06)	5.12 (5.12)
2b	Ph	4-ClC ₆ H ₄	141	29	54.55 (54.63)	3.38 (3.27)	4.57 (4.55)
2c	Ph	4-MeOC ₆ H ₄	133	25	59.34 (59.38)	4.32 (4.32)	4.70 (4.62)
2d	4-ClC ₆ H ₄	4-ClC ₆ H ₄	187	13	48.98 (49.13)	2.68 (2.65)	3.89 (4.09)
2e	4-ClC ₆ H ₄	4-MeOC ₆ H ₄	121	27	53.11 (53.33)	3.52 (3.58)	4.16 (4.15)
2f	4-ClC ₆ H ₄	<i>n</i> -C ₁₁ H ₂₃	104	44	59.40 (59.12)	7.59 (7.31)	3.94 (3.63)

a) Isolated yield based on the starting material, ArCCl₃.Table 2. 3-Substituted 5-Aryl-1,4,2-dithiazolium Perchlorates **3**

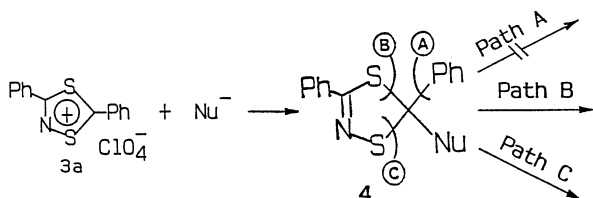
No.	Ar	R	Mp	Yield ^{a)}	Found (Calcd)/%		
			°C	%	C	H	N
3a	Ph	Ph	215	65	46.92 (47.26)	2.77 (2.83)	3.94 (3.94)
3b	Ph	4-ClC ₆ H ₄	216	64	42.96 (43.09)	2.32 (2.31)	3.59 (3.53)
3c	Ph	4-MeOC ₆ H ₄	168	73	46.45 (46.69)	3.22 (3.13)	3.62 (3.63)
3d	4-ClC ₆ H ₄	4-ClC ₆ H ₄	205	78	39.59 (39.59)	1.92 (1.90)	3.33 (3.30)
3e	4-ClC ₆ H ₄	4-MeOC ₆ H ₄	173	60	42.74 (42.87)	2.65 (2.64)	3.36 (3.33)
3f	4-ClC ₆ H ₄	<i>n</i> -C ₁₁ H ₂₃	84	73	48.42 (48.72)	5.82 (5.81)	2.89 (2.99)

a) Isolated yield based on sulfenamides **2**.

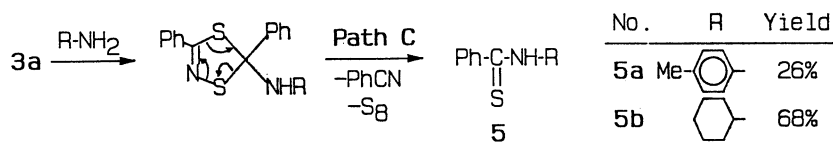
analyses are summarized in Tables 1 and 2.

ArCSS-Na⁺ is also accessible utilizing a common reaction of Grignard reagents (ArMgX) with carbon disulfide. Thus our approach represents a potentially general method for preparing 1,4,2-dithiazolium salts bearing a variety of substituents at C-3 and C-5 positions.

Reaction of 3a with Nucleophiles. We have shown



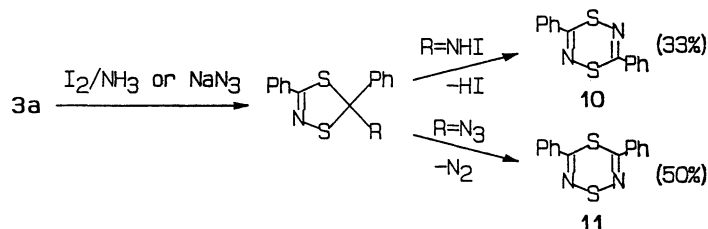
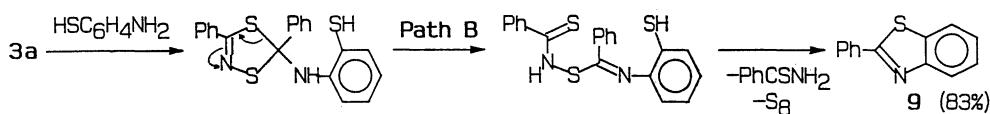
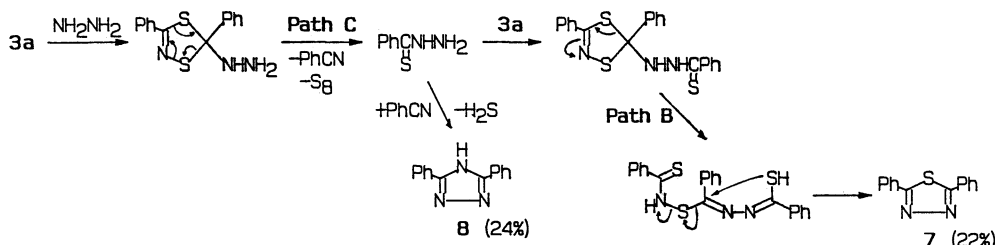
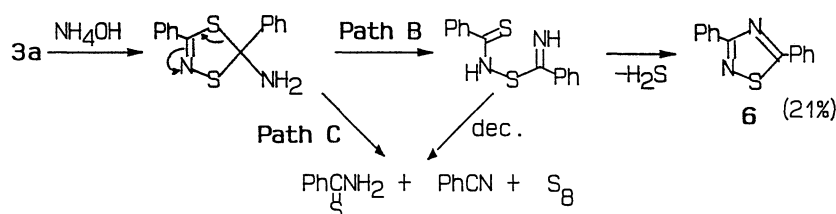
Scheme 2.



Scheme 3.

in our previous papers³⁾ that the reaction of 5-dialkylamino-1,4,2-dithiazolium salts with nucleophiles can be classified into three types (Paths A, B, and C) depending on three possible fission modes (A, B, and C in Scheme 2) of initial adducts (**4**). The reactivity of 5-phenyl-1,4,2-dithiazolium salts was expected to be similar to that of 5-dialkylamino derivatives. However, the possibility of Path A can be ruled out here because the aryl group at C-5 position (the reaction center) has no leaving ability.

When **3a** was allowed to react with various amino compounds, products derived via two reaction courses (Paths B and C) were obtained as expected. A mechanistic interpretation of the formation of products is illustrated in the Schemes and, if necessary, explanation may be offered since a similar reaction manner has been described in detail in our previous paper.^{3a)}

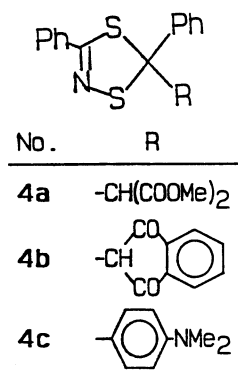


The reaction of **3a** with *p*-toluidine or cyclohexylamine gave *N*-(*p*-tolyl)thiobenzamide (**5a**) (26%) or *N*-(cyclohexyl)thiobenzamide (**5b**) (68%), respectively, together with PhCN and S₈ via Path C (Scheme 3). On treatment with a large excess of aqueous ammonia, **3a** afforded 3,5-diphenyl-1,2,4-thiadiazole (**6**) (21%) via Path B and thiobenzamide (38%) via Path B and/or Path C (Scheme 4). When **3a** was treated with an excess of hydrazine hydrate, the reaction gave not only 2,5-diphenyl-1,3,4-thiadiazole (**7**) (22%) via Path C and the subsequent Path B, but also an unexpected product 3,5-diphenyl-1*H*-1,2,4-triazole (**8**) (24%) (Scheme 5). The formation of **8** seems to result from a side reaction of thiobenzoylhydrazide (PhCSNHNH₂) with PhCN, both of which arose from the initial adduct by ring scission (Path C). A similar reaction of 2-benzoylhydrazinium benzenesulfonate (PhCONH-NH₃⁺ -OSO₂Ph) with benzonitrile leading to **8** is known.⁴⁾ In the case of *o*-aminobenzenethiol, the reaction with **3a** gave 2-phenylbenzothiazole (**9**) (83%) together with thiobenzamide (53%) (Scheme 6). The

formation of **9** is well explained in terms of the similar pathway (Path B) as the latter half in Scheme 5.

In our continuing investigation of the ring expansion reaction of heterocyclic cation compounds by incorporating one nitrogen atom, we recently reported the reaction of **3a** with I₂/aq NH₃ or NaN₃ leading to 3,6-diphenyl-1,4,2,5-dithiadiazine (**10**) in 33% yield or 3,5-diphenyl-1,4,2,6-dithiadiazine (**11**) in 50% yield, respectively (Scheme 7).⁵⁾ This significant difference in selectivity of ring expansion was explained to be due to a contribution of different types of intermediates: nitrenium ion for I₂/aq NH₃ and nitrene for NaN₃.

We have shown in the preceding paper^{3b)} that **3a** is allowed to react with malononitrile, one of highly reactive methylene compounds, in the presence of Et₃N to give 4-cyano-5-phenyl-3-(thiobenzoylamino)-isothiazole in 58% yield via Path B. When reaction of **3a** with other active methylene compounds such as dimethyl malonate and 1,3-indandione in the presence of Et₃N at room temperature was attempted for com-



parison, the initial adducts (**4a** and **4b**) were unexpectedly isolated as the sole products in 33% and 50% yields, respectively. Furthermore, **4a** was unreactive toward stronger bases, e.g., EtONa/EtOH. It is known that malononitrile is often the missing link in the series of active methylene compounds concerning reactivity toward heterocyclic cations;⁶ this tendency was confirmed here again. A similar reaction was observed with *N,N*-dimethylaniline in the absence of base to afford the adduct **4c** in 93% yield. If **4c** is expected to undergo ring cleavage via Path C to give 4-(dimethylamino)thiobenzophenone, **3** can be used as thioaroylating agents for electron-rich aromatic compounds. Barbero et al.⁷ reported a similar approach for acylation of *N,N*-dialkylarylamines by use of 2-substituted 1,3-benzoxathiolium salts.

Experimental

All melting points were uncorrected. ¹H and ¹³C NMR spectra were recorded on a Hitachi R-40 and a JEOL FX-90A spectrometer using TMS as an internal standard. Mass spectra were taken on a Hewlett Packard 5995A spectrometer by electron impact ionizing technique at 70 eV. IR spectra were measured on a JASCO A-302 spectrometer using KBr disks. Commercially available reagents and solvents were used without any purification.

Preparation of *N*-Acyl- and *N*-Aroyl-*S*-thioaroylsulfenamides (2**).** Sodium hydrogensulfide (0.5 mol) was added to an ethanol solution (100 ml) of benzylidene trichloride (**1a**) (0.1 mol). The reaction mixture was refluxed for 10 h. After removal of NaCl and elemental sulfur that deposited from the mixture, chloroform (ca. 60 ml) and water (ca. 60 ml) were added to the solution, which was stirred vigorously. Crude PhCSS-Na⁺ was extracted to the aqueous layer and used directly for the subsequent reaction; the chloroform layer containing unreacted benzylidene trichloride was discarded. Sodium hydroxide (0.15 mol) was dissolved in the ice-cooled aqueous reaction mixture, to which, after addition of ether (ca. 30 ml), an aqueous solution (ca. 30 ml) of hydroxylamine-*O*-sulfonic acid (NH₂OSO₃H) (0.15 mol) was added dropwise under ice-cooling and vigorously stirring conditions over a period of ca. 15 min, during which a dark red color moved from the aqueous to organic layer. Benzoyl chloride (0.11 mol) was added to the vigorously stirred reaction mixture under ice-cooling. The resulting mixture was then allowed to warm to room

temperature and stirred overnight. After evaporation of ether, the resulting precipitate was separated by filtration and was dissolved in hot acetonitrile; any insoluble substances were filtered off. The acetonitrile solution was poured into an aqueous sodium hydrogencarbonate. The precipitate thus formed was collected by filtration and air-dried, which was recrystallized from ethanol. The other sulfenamides **2b–f** were prepared in a similar manner as mentioned above. Their yields, melting points, and elemental analyses are listed in Table 1.

Preparation of 3-Aryl- and 3-Alkyl-5-aryl-1,4,2-dithiazolium Perchlorates (3**).** To an acetic anhydride solution (20 ml) of the *N*-benzoyl-*S*-thiobenzoylsulfenamides (**2a**) (10 mmol), 70% perchloric acid (1 ml) was added dropwise with stirring. The reaction mixture was kept at 60 °C for 2 h and, after cooling, was poured into an excess of ether to give a crude precipitate, which was then recrystallized from acetonitrile. The other dithiazolium perchlorates **3b–f** were also accessible in the same manner as above. Their yields, melting points, and elemental analyses are listed in Table 2.

Reaction of **3a with Amino Compounds: General Procedure.** 3,5-Diphenyl-1,4,2-dithiazolium perchlorate (**3a**) (1 mmol) was added to stirred acetonitrile solutions (6 ml) of amino compounds (2 mmol), except for aqueous ammonia (28%) (4 ml) and hydrazine monohydrate (80%) (0.2 ml). The reaction mixture was stirred for a few hours to 1 d at room temperature. The crude product was extracted with dichloromethane after addition of dil HCl. After the solvent was removed in vacuo, the residue was purified by column chromatography on silica gel with CH₂Cl₂–hexane and recrystallized from appropriate solvents. The yields of products are shown in the Schemes. Products **6**,⁸ **7**,⁹ **8**,⁴ and **9**¹⁰ were identified by direct comparison with each authentic sample.

***N*-(*p*-Tolyl)thiobenzamide (**5a**):** Colorless powder; mp 128.0–129.5 °C (ether–pentane); ¹H NMR (CDCl₃) δ=2.33 (6H, s), 7.1–7.9 (9H, m), and 9.1 (1H, br. s); MS *m/z* (rel intensity) 227 (M⁺, 39), 194 (M⁺–SH, 24), 124 (MeC₆H₄SH⁺, 50), and 121 (PhCS⁺, 100). Found: C, 73.76; H, 5.77; N, 6.17; S, 13.95%. Calcd for C₁₄H₁₃NS: C, 73.97; H, 5.76; N, 6.16; S, 14.10%.

***N*-(Cyclohexyl)thiobenzamide (**5b**):** Colorless powder; mp 86.5–87.0 °C (CH₂Cl₂–hexane); ¹H NMR (CDCl₃) δ=1.2–2.3 (10H, m), 4.3–4.7 (1H, m), 7.3–7.5 (3H, m), 7.55 (1H, br. d), and 7.6–7.8 (2H, m); MS *m/z* (rel intensity) 219 (M⁺, 65), 138 (PhCSNH₂⁺, 62), 121 (PhCS⁺, 100), and 104 (PhCNH⁺, 49). Found: C, 71.22; H, 7.87; N, 6.40; S, 14.57%. Calcd for C₁₃H₁₇NS: C, 71.19; H, 7.81; N, 6.39; S, 14.62%.

Reaction of **3a with Active Methylene Compounds.** 3,5-Diphenyl-1,4,2-dithiazolium perchlorate (**3a**) (1 mmol) was added with stirring to an acetonitrile solution (6 ml) of dimethyl malonate or 1,3-indanedione (1.1 mmol) and triethylamine (2 mmol). The reaction mixture was stirred for 4 h at room temperature. Subsequent work-up and purification were accomplished by a similar procedure with the reaction of **3a** with amino compounds.

5-Bis(methoxycarbonyl)methyl-3,5-diphenyl-1,4,2-dithiazole (4a**):** Yield 33%; oil; ¹H MNR (CDCl₃) δ=3.64 and 3.65 (3H×2, s), 4.70 (1H, s), and 7.2–7.8 (10H, m); ¹³C NMR (CDCl₃) δ=52.58 (q), 52.87 (q), 63.11 (d), 76.55 (s), 126.90 (d), 127.88 (d), 128.04 (d), 128.45 (d), 128.58 (d), 130.53 (d), 132.59 (s), 141.96 (s), 159.19 (s), 166.34 (s), and 166.53 (s); MS *m/z*

(rel intensity) 387 (M^+ , 6), 256 (3,5-diphenyl-1,4,2-dithiazolium cation, 98), 153 ($PhCSS^+$, 100), 121 ($PhCS^+$, 52), and 103 ($PhCN^+$, 21).

2-(3,5-Diphenyl-1,4,2-dithiazol-5-yl)-1,3-indanedione (4b): Yield 50%; pale yellow powder; mp 191.0–192.5 °C (CH_2Cl_2 -hexane); 1H NMR ($CDCl_3$) δ =4.51 (1H, s) and 7.0–8.0 (14H, m); MS m/z (rel intensity) 401 (M^+ , 4), 256 (3,5-diphenyl-1,4,2-dithiazolium cation, 100), 153 ($PhCSS^+$, 74), 121 ($PhCS^+$, 43), and 103 ($PhCN^+$, 21). Found: C, 69.98; H, 3.77; N, 3.59%. Calcd for $C_{23}H_{15}NS_2O_2$: C, 68.81; H, 3.77; N, 3.49%.

Reaction of 3a with *N,N*-Dimethylaniline. Salt **3a** (1 mmol) was added to a stirred acetonitrile solution (6 ml) of *N,N*-dimethylaniline (2 mmol). The reaction mixture was stirred for 4 h at room temperature. Subsequent work-up and purification were accomplished by a similar procedure with the reaction of **3a** with amino compounds.

5-(*p*-Dimethylaminophenyl)-3,5-diphenyl-1,4,2-dithiazole (4c): Yield 93%; oil; 1H NMR ($CDCl_3$) δ =2.88 (6H, s), 6.62 (2H, d, J =9 Hz), 7.2–7.5 (8H, m), 7.5–7.7 (2H, m), and 7.7–7.9 (2H, m); ^{13}C NMR ($CDCl_3$) δ =40.25 (q), 81.99 (s), 111.71 (d), 127.55 (d), 127.91 (d), 127.99 (d), 128.23 (d), 128.47 (d), 128.99 (d), 129.80 (s), 130.32 (d), 133.16 (s), 143.62 (s), 149.68 (s), and 159.30 (s); MS m/z (rel intensity) 376 (M^+ , 14), 273 (M^+ -PhCN, 47), 241 ($Me_2NC_6H_4CSPh^+$, 74), 208 (100), and 164 ($Me_2NC_6H_4CS^+$, 58).

Ring Expansion Reaction of 3a Using $I_2/aq\ NH_3$ System. A large excess of aqueous ammonia (28%) (0.6 ml) was added to a stirred acetonitrile solution (6 ml) of **3a** (1 mmol) and iodine (1 mmol). The reaction mixture was stirred at room temperature until dark red color faded. Subsequent work-up and purification were accomplished by a similar procedure with the reaction of **3a** with amino compounds.

3,6-Diphenyl-1,4,2,5-dithiadiazine (10): Yield 33%; yellow powder; mp 99 °C (CH_2Cl_2 -hexane) (lit.¹¹) 102–104 °C; ^{13}C NMR ($CDCl_3$) δ =128.16 (d), 128.89 (d), 132.17 (d), 134.50 (s), and 169.36 (s); MS m/z (rel intensity) 270 (M^+ , 10), 167 (M^+ -PhCN, 11), 121 ($PhCS^+$, 100), and 103 ($PhCN^+$, 31).

Ring Expansion Reaction of 3a Using NaN_3 . Sodium azide (1.1 mmol) was added to an acetonitrile solution (3 ml) of **3a**. The reaction mixture was stirred for 1 d at room temperature. Subsequent work-up and purification were accomplished by a similar procedure with the reaction of

3a with amino compounds.

3,5-Diphenyl-1,4,2,6-dithiadiazine (11): Yield 50%; orange powder; mp 77 °C (CH_2Cl_2 -hexane) (lit.¹²) 78–80 °C). Spectral data (MS, ^{13}C NMR) were in agreement with those in the literature.

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