October, 1990] © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 2933—2937 (1990) 2933

Preparation and Reactions of 5-Aryl-1,4,2-dithiazolium Salts

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(Received May 22, 1990)

S-Thioaroylsulfenamides ($ArCSSNH_2$), formed by reaction of $ArCSS^-Na^+$ with hydroxylamine-*O*-sulfonic acid, were aroylated or acylated to give *N*-aroyl- or *N*-acyl-*S*-thioaroylsulfenamides, respectively, which were then cyclized with dehydration to afford 3-substituted 5-aryl-1,4,2-dithiazolium salts. The behavior of 3,5-diphenyl-1,4,2-dithiazolium perchlorate toward nucleophiles such as active methylene and amino compounds was studied systematically. The reaction can be classified into two cases depending on fission modes of initial adducts, i.e., ring opening—ring closure reaction (Path B) and fragmentation of dithiazole ring (Path C), and in some cases the initial adducts were isolated.

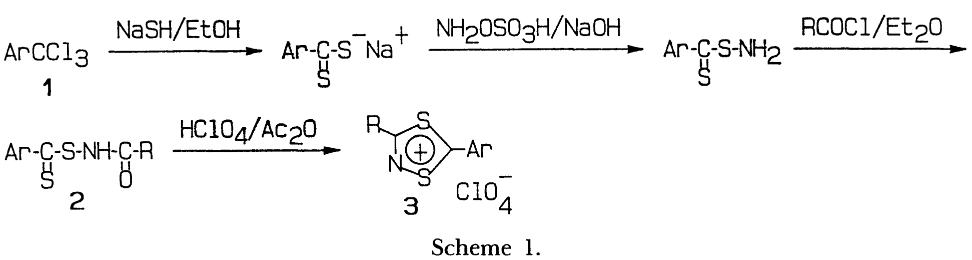
Syntheses of 1,4,2-dithiazolium cations were recently established by three groups independently. 3-Aryl-5-methylthio,[1a)] 3-aryl-5-dialkylamino,[1b,c,e)] 3,5-diaryl,[1b)] and 3,5-bis(dialkylamino)[1e)] derivatives have been prepared so far. Quite recently, Wai and Sammes[1f)] prepared parent ring systems unsubstituted at C-3 and/or C-5 positions. As far as 5-aryl derivatives are concerned, only one example is known; a 3-(4-nitrophenyl)-5-phenyl-1,4,2-dithiazolium salt has been obtained in a low yield by 1,3-dipolar cycloaddition of 4-nitrobenzonitrile sulfide to *o*-ethylthiobenzoate followed by solvolysis.[1d)] On the other hand, our strategy is the aroylation of *S*-dialkylthiocarbamoylsulfenamides followed by dehydration leading to 1,4,2-dithiazolium salts.[1b)] As an extension of our approach, we carried out the aroylation or acylation of *S*-thioaroylsulfenamides and the subsequent dehydration to obtain the 5-aryl derivatives. We now report successful preparation of 3-aryl- and 3-alkyl-5-aryl-1,4,2-dithiazolium salts (**3**) in the initial part.

Generally, five-membered heteroaromatic cation compounds have attracted much attention on their reactivity to serve as versatile intermediates in organic synthesis.[2)] Systematic study on the reactivity of 5-dialkylamino-1,4,2-dithiazolium cations toward nucleophiles such as active methylene and amino compounds has been also reported.[3)] However, the reactivity of 5-aryl-1,4,2-dithiazolium cations has not fully been explored. In our continuing studies on the chemistry of 1,4,2-dithiazolium cations, we have examined systematically the behavior of 3,5-diphenyl-1,4,2-dithiazolium perchlorate (**3a**) toward various nucleophiles.

Results and Discussion

Preparation of 5-Aryl-1,4,2-dithiazolium Salts. *N*-Aroyl- and *N*-acyl-*S*-thioaroylsulfenamides (**2**), the precursors for **3**, were obtained from aryltrichloromethanes ($ArCCl_3$, **1**) as shown in Scheme 1, which was accomplished in a "one pot" procedure. $ArCCl_3$ was allowed to react with an excess of sodium hydrogensulfide in EtOH to give $ArCSS^-Na^+$, which, on treatment with hydroxylamine-*O*-sulfonic acid (NH_2OSO_3H) in aqueous sodium hydroxide, was converted into *S*-thioaroylsulfenamides ($ArCSSNH_2$). The in situ generated $ArCSSNH_2$ was directly aroylated with aroyl chlorides to afford **2a—e**. *N*-Lauroyl-*S*-thiobenzoylsulfenamide (**2f**) was also prepared in 44% yield according to the same procedure as for **2a—e**. $ArCSSNH_2$ had better be used for the aroylation or acylation without isolation because of its poor stability, whereas the aroylated derivatives **2** are stable enough to be stored in air at room temperature for months. The IR spectrum of **2a** exhibited N-H and C=O absorption bands at 3150 and 1655 cm^{-1}, respectively. The mass spectrum of **2a** showed a molecular ion peak and fragmentation pattern ($PhCS^+$ $PhCO^+$, etc.) in line with the proposed structure.

The resulting sulfenamide derivatives **2** were treated with a strong acidic media, e.g., 70% $HClO_4$, to undergo cyclization with dehydration leading to yellow crystalline products **3a—f** in good yields. The IR spectrum of **3a** indicated the presence of ClO_4^- at 1083 cm^{-1} and the mass spectrum showed the fragment corresponding to the dithiazolium cation at *m/z* 256. Their melting points, yields, and elemental



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$_4$	*n*-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, ArCCl$_3$.

Table 2. 3-Substituted 5-Aryl-1,4,2-dithiazolium Perchlorates **3**

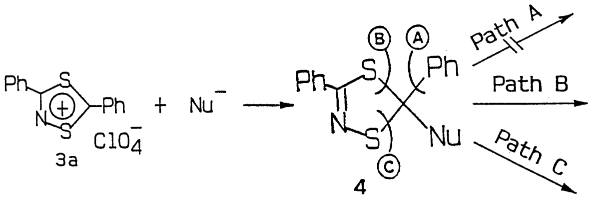
No.	Ar	R	Mp	Yield[a)]	Found (Calcd)/%		
			°C	%	C	H	N
3a	Ph	Ph	215	65	46.92 (47.26)	2.77 (2.83)	3.94 (3.94)
3b	Ph	4-ClC$_6$H$_4$	216	64	42.96 (43.09)	2.32 (2.31)	3.59 (3.53)
3c	Ph	4-MeOC$_6$H$_4$	168	73	46.45 (46.69)	3.22 (3.13)	3.62 (3.63)
3d	4-ClC$_6$H$_4$	4-ClC$_6$H$_4$	205	78	39.59 (39.59)	1.92 (1.90)	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$_4$	*n*-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.

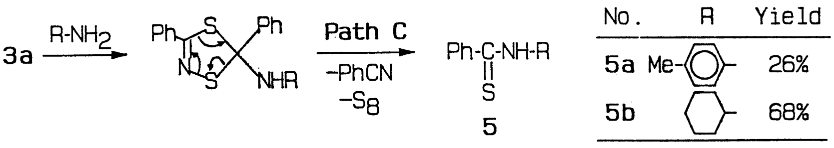
ArCSS$^-$Na$^+$ is also accessible utilizing a common reaction of Grignard reagents (ArMgX) with carbon disulfide. Thus our approach represents a potentially general method for preparing 1,4,2-dithiazolium salts bearing a variety of substituents at C-3 and C-5 positions.

Reaction of 3a with Nucleophiles. We have shown in our previous papers[3)] 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.

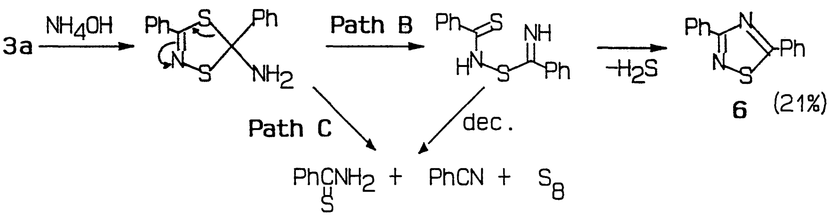


Scheme 2.

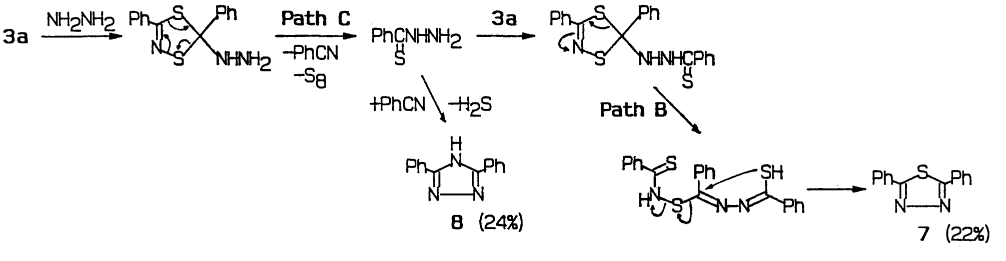
When **3a** was allowed to react with various amino compounds, products derived via two reaction courses (Paths B and C) were obtained as expected. A mechanistic interpretation of the formation of products is illustrated in the Schemes and, if necessary, explanation may be offered since a similar reaction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



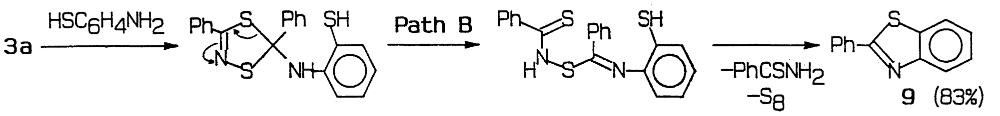
Scheme 3.



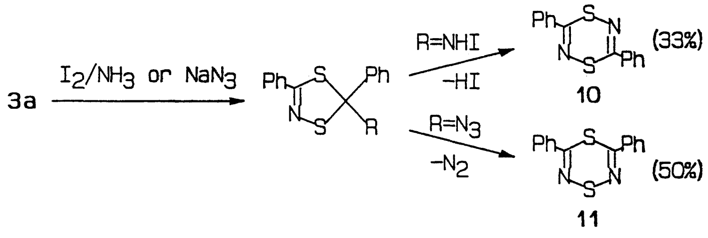
Scheme 4.



Scheme 5.



Scheme 6.

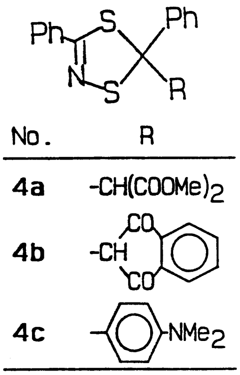


Scheme 7.

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 S_8 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-dipheny-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 ($PhCSNHNH_2$) with PhCN, both of which arose from the initial adduct by ring scission (Path C). A similar reaction of 2-benzoylhydrazinium benzenesulfonate ($PhCONH\text{-}NH_3^+\ {}^-OSO_2Ph$) 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 I_2/aq NH_3 or NaN_3 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 I_2/aq NH_3 and nitrene for NaN_3.

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 Et_3N 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 Et_3N 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. ^{1}H and ^{13}C 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 benzylidyne 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 benzylidyne 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 (NH_2OSO_3H) (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 CH_2Cl_2-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); ^{1}H NMR ($CDCl_3$) 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 ($MeC_6H_4SH^+$, 50), and 121 ($PhCS^+$, 100). Found: C, 73.76; H, 5.77; N, 6.17; S, 13.95%. Calcd for $C_{14}H_{13}NS$: C, 73.97; H, 5.76; N, 6.16; S, 14.10%.

***N*-(Cyclohexyl)thiobenzamide (5b):** Colorless powder; mp 86.5—87.0 °C (CH_2Cl_2-hexane); ^{1}H NMR ($CDCl_3$) 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 ($PhCSNH_3^+$, 62), 121 ($PhCS^+$, 100), and 104 ($PhCNH^+$, 49). Found: C, 71.22; H, 7.87; N, 6.40; S, 14.57%. Calcd for $C_{13}H_{17}NS$: 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; ^{1}H MNR ($CDCl_3$) δ=3.64 and 3.65 (3H×2, s), 4.70 (1H, s), and 7.2—7.8 (10H, m); ^{13}C NMR ($CDCl_3$) 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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