Reaction of 1,4,2-Dithiazolium Salts with Amino Compounds

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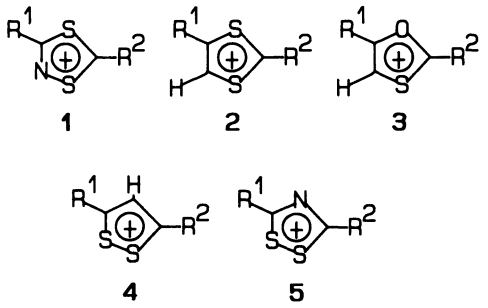
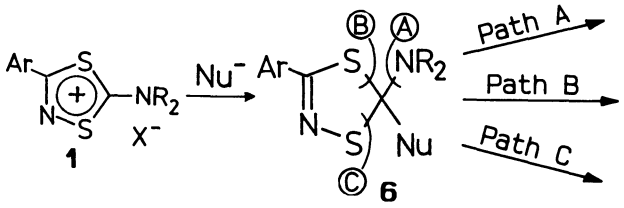
Systematic studies on the behavior of 1,4,2-dithiazolium cations (**1**) toward various amino compounds (ammonia, aliphatic and aromatic amines, hydrazine, semicarbazide, thiosemicarbazide derivatives, etc.) were performed. The reaction pathway could be classified into three types depending on possible three fission modes of the initially-formed adduct. The main products were 5-imino-1,4,2-dithiazole, thiourea, and 1,3,4-thiadiazole derivatives, through the three different pathways, respectively. In order to clarify the factors controlling the reaction courses, the reactions of **1** with *p*-substituted aniline derivatives were carried out under systematically varying conditions. The strength of bases and the polarity of solvents had clear influence on the reactivity. The reaction mechanism is also discussed.

Chemistry of five-membered heteroaromatic cations, which are stabilized by 6 π-electron system satisfying Hückel's rule, has been extensively studied and reviewed. These cations have attracted much attention to their reactivity as potentially versatile intermediates for a wide range of heterocyclic compounds involving sulfur and/or nitrogen atoms. In particular, the reactivity of 1,3-dithiolium (**2**)[1] or 1,3-oxathiolium cations (**3**)[2] toward nucleophiles such as active methylene and amino compounds has been the subject of detailed investigations. Convenient synthetic methods for 1,2-dithiolium (**4**)[3] and 1,2,4-dithiazolium cations (**5**)[4] and their reactions with a number of active methylene compounds have been also reported. On the other hand, chemistry of 1,4,2-dithiazolium cations (**1**), aza-analogues of **2** as well as isomeric ring system of **5**, has not been fully explored. The synthesis of **1** was recently established by Paton,[5] Sammes,[6] and the authors.[7] Some reactions of **1** with nucleophiles were also attempted.[5,6b] However, no systematic study on the reactivity of **1** has been reported. In our continued investigation on the chemistry of 1,4,2-dithiazolium cations (**1**), we have examined systematically the behavior of **1** toward various amino compounds.



Results and Discussion

The reaction of **1** with amino compounds took place by initial attack of the terminal nitrogen of nucleophiles at the C-5 position of cations **1**, leading to the intermediate adducts (**6**) (Scheme 1), analogously to the case for **2** or **3**. However, the subsequent



Scheme 1.

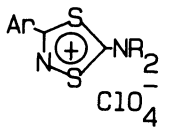
pathway from this stage was unique and can be classified into the following three types depending on possible three fission modes (A, B, and C in Scheme 1).

Path A: Proton abstraction by base followed by liberation of dialkylamino group to give 5-imino-1,4,2-dithiazole derivatives.

Path B: Loss of proton results in, in turn, the C–S bond cleavage to afford an open-chain intermediate, which then undergoes either recyclization or decomposition leading to final products.

Path C: Spontaneous fragmentation of dithiazole ring to form thiourea derivatives together with nitrile and sulfur.

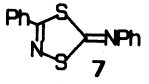
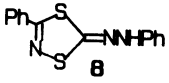
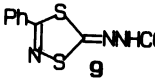
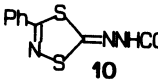
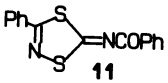
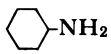
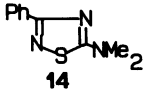
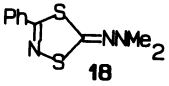
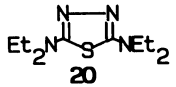
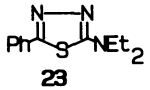
The reaction conditions, products (classified according to these three pathways), and their yields are summarized in Table 1.



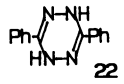
No.	Ar	NR_2
1a	Ph	NMe_2
1b	"	NEt_2
1c	"	molpholino
1d	"	NPhMe
1e	4-ClC_6H_4	NEt_2
1f	4-MeC_6H_4	"
1g	4-$MeOC_6H_4$	"

When 1,4,2-dithiazolium salt (**1a**) was allowed to react with aniline (Entry 1), hydrazine derivatives (Entries 2—4), and benzoylsulfenamide (Entry 5) in the absence of base, the sole formation of the correspond-

Table 1. The Reaction of 1,4,2-Dithiazolium Salts **1** with Various Amino Compounds

Entry	NR_2 of **1**	Amino compd	Solvent	Base	Time	Temp	Product (Yield/%)[a] path A	path B[b]	path C
1	NMe_2	$PhNH_2$	MeCN	—	6 h	refl.	 **7** (90)	—	—
2	NMe_2	$PhNHNH_2$	CH_2Cl_2	—	1 h	refl.	 **8** (88)	—	—
3	NMe_2	$PhCONHNH_2$	CH_2Cl_2	—	0.5 h	refl.	 **9** (87)	—	—
4	NMe_2	$PhNHCONHNH_2$	CH_2Cl_2	—	0.5 h	refl.	 **10** (80)	—	—
5	NMe_2	$PhCOSNH_2$	MeCN	—	3 d	r.t.	 **11** (29)	—	—
6	NMe_2		MeCN	—	2 h	r.t.	—	—	 **12** (88)
7	NMe_2	$Ph_2S{\rightarrow}NH$	MeCN	—	2 h	r.t.	—	—	$Me_2NCSN{\leftarrow}SPh_2$ **13** (33)
8	NMe_2	NH_4OH	H_2O	—	0.5 d	r.t.	—	 **14** (1)	Me_2NCSNH_2 **16** (62)
9	NMe_2	Me_2NNH_2	CH_2Cl_2	—	0.5 h	refl.	 **18** (29)	—	$Me_2NCSNHNMe_2$ **19** (18)
10	NEt_2	$NH_2NH_2{\cdot}H_2O$	H_2O	—	2 h	r.t.	—	 **20** (43)[b,c]	—
11	NEt_2	$Et_2NCSNHNH_2$	H_2O	Et_3N	0.5 h	r.t.	—	**20** (63)	—
12	NEt_2	$PhCSNHNH_2$	MeCN	Et_3N	1 h	r.t.	—	 **23** (78)	—
13	NMe_2	$PhCONHNH_2$	MeCN	Et_3N	1 h	r.t.	—	—	$Me_2NCSNHNHCOPh$ **24** (49)

a) Isolated yield. b) Conversion yield based on **1b**. c) 3,6-Diphenyl-1,4-dihydro-1,2,4,5-tetrazine **22** was also obtained in 3% yield. d) Thiobenzamide **15** was formed via Path B (Entries 8—12): 27% (Entry 8), 18% (Entry 9), 30% (Entry 10), 55% (Entry 11), 84% (Entry 12).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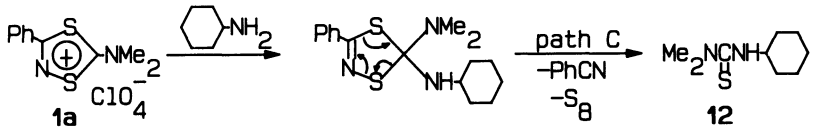
ing 3-phenyl-5-substituted imino-1,4,2-dithiazoles (**7**—**11**) (via Path A) was observed. In the case of Entry 5, extrusion of sulfur from sulfenamide moiety simultaneously proceeded. On the other hand, the reaction of **1** with other *N*-unsubstituted sulfenamides such as *S*-dimethylthiocarbamoyl substituted sulfenamide did not give this type of compounds, but afforded 1,4,2,5-dithiadiazine derivatives, arising from ring expansion on nitrogen atom.[8]

The reaction of **1a** with cyclohexylamine (Entry 6) and *S,S*-diphenylsulfilimine (Entry 7) gave *N*-cyclohexyl-*N'*,*N'*-dimethylthiourea (**12**) and *N*-(dimethylthiocarbamoyl)-*S,S*-diphenylsulfilimine (**13**), respectively, together with benzonitrile and sulfur via Path C (Scheme 2).

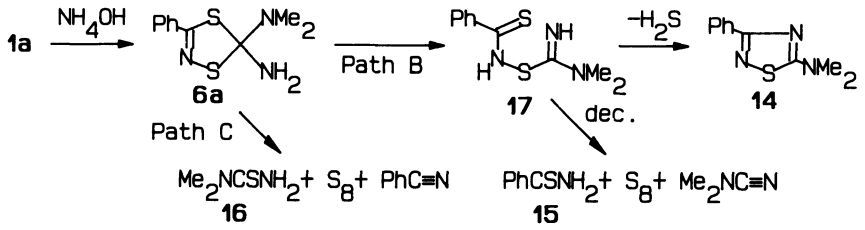
On treatment with a large excess of aqueous ammonia (Entry 8), **1a** yielded not only *N,N*-dimethylthiourea (**16**) (via Path C) but 5-dimethylamino-3-phenyl-1,2,4-thiadiazole (**14**) and thiobenzamide (**15**) (both via Path B). The formation of **14** and **15** can be rationalized as follows. The initially-formed adduct **6a** (Scheme 3) opens the ring (via Path B) to form the second intermediate **17**, which then undergoes either ring closure reaction accomplished by elimination of H_2S or decomposition reaction, to give final products **14** and **15**, respectively. Furthermore, when treated with *N,N*-dimethylhydrazine (Entry 9), **1a** gave three types of products, i.e., dithiazole derivative (**18**) (via Path A), thiobenzamide (**15**) (via Path B), and thiourea derivative (**19**) (via Path C).

In the case of an excess of hydrazine hydrate (Entry 10), the reaction with **1b** gave an unexpected product 2,5-bis(diethylamino)-1,3,4-thiadiazole (**20**) togther with thiobenzamide (**15**). A mechanistic interpretation for the formation of **20** is shown in Scheme 4. The intermediate adduct by the reaction of **1b** with NH_2NH_2 undergoes ring scission to provide *N,N*-diethylthiosemicarbazide (**21**) (via Path C), which then reacts with another molecule of **1b** as a nucleophile to afford the alternative adduct **6b** followed by ring opening (via Path B) and ring closure reaction with liberation of **15** and sulfur to give the final product **20**. The reason why **1b** reacts exclusively with **21** even in the presence of an excess of hydrazine hydrate seems to be as follows. **1b** is almost insoluble in water and the reaction of **1b** with hydrazine proceeds slowly. Thus, the crystalline **1b** reacts preferentially with oily **21** free from water in contrast with NH_2NH_2 in aqueous solution. The concomitant formation of 3,6-diphenyl-1,4-dihydro-1,2,4,5-tetrazine (**22**) in 3% yield seems to result from a side reaction of PhCN with NH_2NH_2. In order to confirm this latter pathway, the reaction of **1b** with **21** (Entry 11) was carried out in the presence of triethylamine in aqueous solution. The reaction also gave **20** in a good yield.

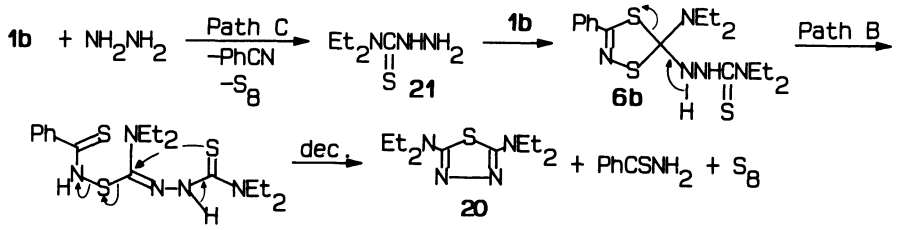
A similar reaction was observed with thiobenzoylhydrazine (Entry 12) in the presence of Et_3N to give



Scheme 2.



Scheme 3.



Scheme 4.

Table 2. ^{1}H NMR, IR, MS, Mp, and Elemental Analysis for the Products

Compd	^{1}H NMR ($CDCl_3$)[a]	IR (KBr) cm^{-1}
8	6.16 (1H, s), 6.8—7.6 (8H, m), 7.7—7.9 (2H, m)	1599, 1491, 1244, 928
9	7.3—7.6 (6H, m), 7.7—7.9 (2H, m), 7.9—8.1 (2H, m), 10.6 (1H, br. s)	1628, 1522, 1286, 926
10	6.6—6.8 (1H, m), 6.9—7.1 (2H, m), 7.2—7.4 (5H, m), 7.4—7.6[b] (2H, m), 8.5 (1H, br. s), 9.5 (1H, br. s)	3372, 1673, 1529, 1114
11	7.5—7.7 (6H, m), 7.9—8.1 (2H, m), 8.3—8.5 (2H, m)	1606, 1421, 1315, 1281
12	0.9—2.3 (10H, m), 3.26 (6H, s), 4.3 (1H, br. s)	1593, 1389, 1010, 603
18	2.60 (6H, s), 7.4—7.6 (3H, m), 7.7—7.9 (2H, m)	1556, 1653, 1232, 948
19	2.68 (6H, s), 3.23 (6H, s)	3184, 1543, 1004, 1115
20	1.20 (12H, t, J=7.2Hz), 3.39 (8H, q, J=7.2Hz)	1508, 1431, 1367, 736
22	5.70 (2H, s), 7.5—7.6 (6H, m), 8.0—8.2 (4H, m)	1473, 1444, 769, 699
23	1.27 (6H, t, J=7.0Hz), 3.56 (4H, q, J=7.0Hz), 7.3—7.5 (3H, m), 7.8—8.0 (2H, m)	1529, 1452, 1350, 1307
24	3.35 (6H, s), 7.4—7.6 (3H, m), 7.8—8.0 (2H, m), 8.8 (1H, br. d), 10.1 (1H, br. d)	3260, 3200, 1652, 1524

Compd	MS (rel. intensity) m/z	Mp θ_m (solv.) °C	Found (Calcd)/% C	H	N	S
8	285 (M^+, 16), 103 (100)	136.5—137.0 ($CHCl_3$-MeCN)	58.79 (58.92)	3.81 (3.89)	14.85 (14.72)	22.55 (22.47)
9	313 (M^+, 9), 105 (100)	134.0—135.0 ($CHCl_3$-MeCN)	57.45 (57.49)	3.50 (3.54)	13.62 (13.41)	20.40 (20.46)
10	328 (M^+, 9), 103 (77)	186.5—187.0 (DMSO)	54.65 (54.86)	3.68 (3.68)	17.15 (17.06)	19.37 (19.52)
11	298 (M^+, 4), 105 (100)	191.5—192.0 (CH_2Cl_2-MeCN)	60.18 (60.38)	3.32 (3.38)	9.37 (9.39)	21.49 (21.49)
12	186 (M^+, 100), 88 (88)	91.5—92.0 (CH_2Cl_2-pentane)	58.19 (58.02)	9.74 (9.74)	15.04 (15.04)	17.24 (17.21)
18	237 (M^+, 45), 135 (27)	78.5—79.0 (CH_2Cl_2-pentane)	50.63 (50.61)	4.67 (4.67)	17.72 (17.70)	27.05 (27.02)
19	147 (M^+, 59), 88 (100)	88.5—89.0 (CH_2Cl_2-pentane)	40.73 (40.79)	8.79 (8.90)	28.46 (28.54)	21.78 (21.77)
20	228 (M^+, 100), 116 (27)	52.5—53.0 (Pentane-Et_2O)	52.35 (52.60)	8.74 (8.83)	24.40 (24.53)	14.00 (14.04)
22	236 (M^+, 44), 104 (100)	263.5—264.5 (CH_2Cl_2-Et_2O)	70.92 (71.17)	5.11 (5.12)	23.66 (23.71)	
23	233 (M^+, 76), 190 (100)	43.0—44.0 (Pentane)	61.75 (61.77)	6.48 (6.48)	18.03 (18.01)	13.80 (13.74)
24	223 (M^+, 28), 88 (100)	164.5—165.0 (MeCN)	53.80 (53.79)	5.87 (5.87)	18.89 (18.82)	14.39 (14.36)

a) ppm from internal TMS. b) In DMSO-d_6.

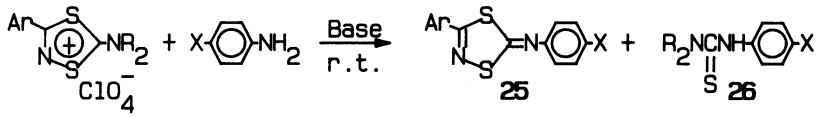
2-diethylamino-5-phenyl-1,3,4-thiadiazole (**23**) in a good yield via the same pathway (Path B) mentioned above. On the other hand, on treatment with its oxa-analogue, benzoylhydrazine, **1a** gave only a product **9** in the absence of base (via Path A) (Entry 3), whereas, in the presence of Et_3N (Entry 13), **1a** afforded 4-benzoyl-1,1-dimethylthiosemicarbazide (**24**) (via Path C).

From the above results, the basicity of reaction solution as well as the nature of nucleophiles seem to be important factors determining the reaction modes. In order to get additional information on the factors controlling the three reaction courses, we selected the combination of **1a—g** with *p*-substituted anilines to examine the reaction under various conditions (Table 3).

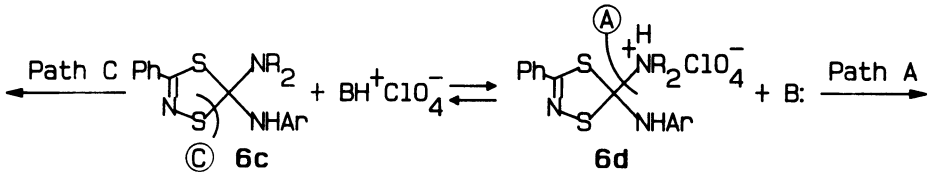
First of all, to explore the effects of base strength, the reaction of **1a** with *p*-toluidine was examined in the presence of four different bases and in the absence of base. It was found that the formation of *N,N*-dimethyl-*N'*-(*p*-tolyl)thiourea (**26e**) (via Path C) predominates in comparison with that of 5-(*p*-tolyl)imino-3-phenyl-1,4,2-dithiazole (**25e**) (via Path A) with increasing value of pK_a (Entries 14—18); the ratio between the two products varies widely. Toluidine itself (pK_a 5.09) can act as a base, although its basicity is lower than that of pyridine. A similar trend was evident in the reaction of **1b** with *p*-toluidine (Entries 19—21). Furthermore, even when triphenylphosphine was used instead of amine base, **26** was produced selectively (Entries 22, 23).

These results can be interpreted as follows. Attack

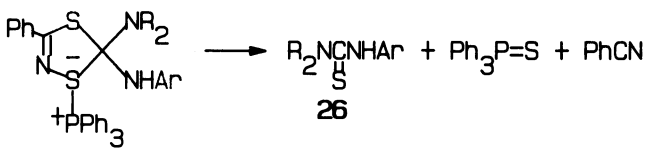
Table 3. The Reaction of **1** with *p*-Substituted Aniline Derivatives



Entry	NR_2	Ar	X	Base (pK_a)	Solvent (ε_γ)	Yield/%	
						25	**26**
14	NMe_2	Ph	Me	—	MeCN	71	—
15	NMe_2	Ph	Me	Pyridine (5.19)	MeCN	73	18
16	NMe_2	Ph	Me	γ-Picoline (6.02)	MeCN	73	24
17	NMe_2	Ph	Me	2,6-Lutidine (6.72)	MeCN	42	44
18	NMe_2	Ph	Me	Triethylamine (10.9)	MeCN	—	64
19	NEt_2	Ph	Me	Pyridine	MeCN	53	Tr.
20	NEt_2	Ph	Me	γ-Picoline	MeCN	48	38
21	NEt_2	Ph	Me	2,6-Lutidine	MeCN	15	48
22	NMe_2	Ph	Me	Ph_3P	MeCN	Tr.	45
23	NMe_2	Ph	Me	Ph_3P	CH_2Cl_2	—	53
24	NEt_2	4-ClC_6H_4	Me	γ-Picoline	MeCN	42	50
25	NEt_2	Ph	Me	γ-Picoline	MeCN	48	38
26	NEt_2	4-MeC_6H_4	Me	γ-Picoline	MeCN	53	32
27	NEt_2	4-$MeOC_6H_4$	Me	γ-Picoline	MeCN	41	29
28	NMe_2	Ph	Me	γ-Picoline	MeCN	48	38
29	NEt_2	Ph	Me	γ-Picoline	MeCN	73	24
30	Morpholino	Ph	Me	γ-Picoline	MeCN	44	8
31	NPhMe	Ph	Me	γ-Picoline	MeCN	85	11
32	NMe_2	Ph	Me	γ-Picoline	CH_2Cl_2 (9.1)	93	7
33	NMe_2	Ph	Me	γ-Picoline	EtOH (27.0)	81	13
34	NMe_2	Ph	Me	γ-Picoline	MeCN (37.5)	73	24
35	NMe_2	Ph	Me	γ-Picoline	DMSO (46.7)	50	47
36	NMe_2	Ph	MeO	γ-Picoline	MeCN	72	20
37	NMe_2	Ph	Me	γ-Picoline	MeCN	73	24
38	NMe_2	Ph	Cl	γ-Picoline	MeCN	42	23



Scheme 5.



Scheme 6.

of *p*-toluidine on the C-5 position of **1** leads to intermediate **6c** which is in equilibrium with **6d** as shown in Scheme 5. The equilibrium is shifted toward **6c** in the presence of a stronger base by effective trapping of perchloric acid, and hence fragmentation of **6c** proceeds preferentially to afford **26** (via Path C). On the other hand, in the presence of a weaker base, considerable contribution of **6d** leads to the pre-

ferential liberation of dialkylamino group to give **25** (via Path A). In the case of phosphine, nucleophilic attack by Ph_3P on the sulfur atom (1- or 4-position) of adduct **6c** promotes the sulfur extrusion resulting in the preferential formation of **26**; triphenylphosphine sulfide was also formed as expected.

In order to examine the influence of substituents in 1,4,2-dithiazolium cations (**1**), the reactions of **1a—g**, bearing different aryl groups at the C-3 position (Entries 24—27) and different di-substituted amino groups at the C-5 position (Entries 28—31), with *p*-toluidine in the presence of γ-picoline were carried out. The yields and the ratio of products **25** and **26** depend mainly on the substituents at the C-5 position which is the reaction center, but almost negligible dependence upon those at C-3 was found. According to the rationalization mentioned above, the equilibrium should be shifted toward **6d** (Scheme 5) with high basicity of the di-substituted amino groups at C-5. Therefore, the formation of **25** should be favored. However, the fact obtained stands in contrast to this expected result. It may be attributable to an extra factor: a liberating secondary amine from **6d**, in turn, acts as a base. The increasing order of basicity of the corresponding secondary amines is known as follows: $Et_2NH \approx Me_2NH > O(C_2H_4)_2NH > PhMeNH$.[9] Thus, in the case where the liberating amine has relatively strong basicity (e.g. Me_2NH and Et_2NH), the yield of **26** somewhat increased.

When the reaction was carried out in four different solvents (Entries 32—35), the selectivity proved to be clearly solvent-dependent, where the ratio of **25** to **26** decreased linearly with increase in dielectric constant (ε_γ). It could be postulated that adduct **6** tends to cleave in polar solvents, probably because the transition state in the ring scission reaction has some

Table 4. Characterization Data of Compounds **25**

No.	Ar	X	^{1}H NMR ($CDCl_3$, ppm from TMS)	MS (rel. intensity) *m/z*	Mp θ_m/°C
25a	4-ClC_6H_4	Me	2.37 (3H, m), 6.98, 7.24 (2H, d, *J*=9Hz), 7.43, 7.72 (2H, d, *J*=9Hz)	320 (M^++2, 6.2), 318 (M^+, 14.7), 181 (100)	128.0—130.0
25b	4-MeC_6H_4	Me	2.37 (3H, s), 2.39 (3H, s), 6.99, 7.23 (2H, d, *J*=9Hz), 7.25, 7.66 (2H, d, *J*=9Hz)	298 (M^+, 12), 181 (61), 149 (100)	128.0—129.5
25c	4-$MeOC_6H_4$	Me	2.36 (3H, s), 3.84 (3H, s), 6.95, 7.24 (2H, d, *J*=9Hz), 6.9—7.1, 7.6—7.8 (2H, m)	314 (M^+, 12), 165 (100), 133 (48)	128.0—128.5
25d	Ph	Cl	7.04, 7.33 (2H, d, *J*=9Hz), 7.4—7.6 (3H, m), 7.7—7.9 (2H, m)	306 (M^++2, 3.5), 304 (M^+, 7.6), 135 (100)	129.0—129.5
25e	Ph	Me	2.36 (3H, s), 6.99, 7.24 (2H, d, *J*=9Hz), 7.4—7.6 (3H, m), 7.7—7.9 (2H, m)	284 (M^+, 19), 181 (100), 135 (95)	88.0—88.5
25f	Ph	MeO	3.83 (3H, s), 6.9—7.2 (4H, m), 7.4—7.6 (3H, m), 7.7—7.9 (2H, m)	300 (M^+, 18), 165 (77), 133 (100)	124.0—125.0

Table 5. Characterization Data of Compounds **26**

No.	R_2N	X	^{1}H NMR ($CDCl_3$, ppm from TMS)	MS (rel. intensity) *m/z*	Mp θ_m/°C
26a	Et_2N	Me	1.27 (6H, t, *J*=7.2Hz), 2.33 (3H, s), 3.75 (4H, q, *J*=7.2Hz), 7.17 (4H, s)	222 (M^+, 49), 189 (23), 116 (100)	Oil
26b	Morpholino	Me	2.32 (3H, s), 3.6—3.9 (8H, m), 7.0—7.2 (4H, m)	236 (M^+, 65), 130 (66), 86 (100)	141.5—143.0
26c	PhMeN	Me	2.30 (3H, s), 3.74 (3H, s), 7.16 (4H, s), 7.3—7.7 (5H, m)	256 (M^+, 65), 150 (100), 106 (100)	116.5—117.5
26d	Me_2N	Cl	3.06 (6H, s), 6.62, 7.12 (2H, d, *J*=9Hz)	216 (M^++2, 9), 214 (M^+, 24), 88 (100)	150.0—151.5
26e	Me_2N	Me	2.33 (3H, s), 3.33 (3H, s), 7.17 (4H, s)	194 (M^+, 42), 91 (33), 88 (100)	166.0—167.0
26f	Me_2N	MeO	3.29 (6H, s), 3.80 (3H, s), 6.88, 7.20 (2H, d, *J*=9Hz)	210 (M^+, 33), 121 (11), 88 (100)	121.5—122.0

polar character and scission energy is reduced in polar media.

Finally, the reactions of **1** with aniline derivatives bearing different substituents X (MeO, Me, and Cl) at the para-position were examined (Entries 36—38). However, the substituents X showed little effect on both the yields and the ratio of **25** to **26**. For definite interpretation on the factors which favor Path B, further detailed information will be needed.

In summary, the reactivity of 1,4,2-dithiazolium cations (**1**) proved to be partly similar to that of 1,3-dithiolium cations (**2**)[1] or 1,3-oxathiolium cations (**3**)[2] (Path A and a part of Path B), but partly different from that of all of other five-membered heteroaromatic cations[1-4] (Path C and a part of Path B). The reaction of **1** with various active methylene compounds has currently been studied; the results will be reported in a separate paper.

Experimental

All the melting points were uncorrected. The ^{1}H NMR spectra were recorded on a Hitachi R-40, in $CDCl_3$, using TMS as an internal standard. The IR spectra were measured on a JASCO A-302 spectrometer using KBr disks. The low-resolution mass spectra were taken on Hewlett Packard 5995A spectrometer by electron impact ionizing technique at 70 eV.

1,4,2-Dithiazolium salts (**1**),[7] *S*-benzoylsulfenamide,[10] *N*,*N*-diethylthiocarbazide (**21**),[11] and thiobenzoylhydrazine[12] were prepared according to the procedures in the literatures. Other reagents were commercially available and used without any purification.

Reaction of 1a, b with Amino Compounds; General Procedure. 1,4,2-Dithiazolium perchlorates **1a,b** (1 mmol) were added to stirred solutions (6 ml) of amino compounds (2 mmol), except for aqueous ammonia (28%) (4 ml) (Entry 8) and hydrazine monohydrate (80%) (0.2ml) (Entry 10). In the case of using base, the combination of **1** (1 mmol), amino compounds (1 mmol), and triethylamine (1 mmol) was adopted (Entries 11—13). Other reaction conditions were listed in Table 1. After the solvent was removed in vacuo, the residue was purified by column chromatography on silica gel and recrystallization from appropriate solvents listed in Table 3. The yields of products are presented in Table 1 and their characterization data are shown in Table 3. On the other hand, **7**,[5] **13**,[13] **14**,[14] and **16**[15] were identified by direct comparison with each authentic sample.

Reaction of 1a—g with *p*-Substituted Aniline Derivatives. 1,4,2-Dithiazolium perchlorates (**1a—g**) (1 mmol) were added to stirred solutions (4 ml) of the aniline derivatives (1.1 mmol) in the presence of base (1.1 mmol). The reaction mixture was stirred for 6 h at room temperature. The crude products were extracted with dichloromethane (20 ml×2) after addition of 2% hydrochloric acid. The two products **25** and **26** were isolated by preparative TLC. Their mps and spectral data are shown in Tables 4 and 5. The elemental analyses of **25e** and **26e** are shown below. Identification of other **25** and **26**'s was based only on spectral data.

25e: Found: C, 63.18; H, 4.21; N, 9.75%. Calcd for $C_{15}H_{12}N_2S_2$: C, 63.35; H, 4.25; N, 9.85%.

26e: Found: C, 61.71; H, 7.28; N, 14.37%. Calcd for $C_{10}H_{14}N_2S$: C, 61.82; H, 7.26; N, 14.42%.

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