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THE REACTION OF 3-METHYLTHIAZOLIUM DERIVATIVES WITH SUPEROXIDE

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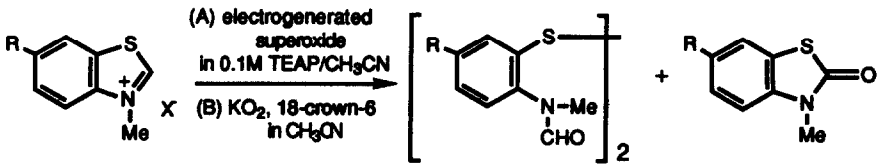
Abstract: 3-Methylbenzothiazolium salts were allowed to react with superoxide to afford dimeric bis[*o*-(*N*-formyl-*N*-methylamino)phenyl]disulfides and 3-methyl-2-benzothiazolones. The reaction was applied to monocyclic thiazolium salts, and novel ten-membered ring compounds were formed whose structures were elucidated by X-ray crystallographic analysis. These results prompted us to alternative synthesis of the ring compound, and bithiazolium salts were revealed to afford them by the reaction with superoxide.

Thiazolium cations,[1] which are active moieties of thiamine, have received considerable attentions from both chemical and biological viewpoints. Especially, the reactivities of C-2 acidic protons and the intermediates formed by the proton elimination have been the controversial matters up to now.[2] It was reported by Metzger *et al.* that 3-methylbenzothiazolium salt **1** was treated with base such as triethylamine to give bi(3-methylbenzothiazolinylidene),[3] whereas electroreduction of **1** afforded bi(3-methylbenzothiazolinyl).[4]

During our study of the reaction of heterocycles with superoxide,[5] we directed our attention to such diverse reactivities of **1**. Superoxide, which is one of the most noteworthy active oxygens,[6] has a variety of chemical reactivities including proton abstraction,[7] one electron reduction,[8] oxidation,[9] nucleophilic reaction.[10] Thus the interaction of **1** with superoxide was of interest with respect to both multi-reactivities. In this paper, we wish to report the detailed results[11] of the reaction of thiazolium salts with superoxide, which afforded specific products for superoxide.

At first, 3-methylbenzothiazolium salt **1** was allowed to react with potassium superoxide in the presence of 18-crown-6 in acetonitrile, and it was revealed that bis[2-(*N*-formyl-*N*-methylamino)phenyl]disulfide **2**[12] was obtained accompanied by 3-methyl-2-benzothiazolone **3** (Scheme 1 and Table I, method B). The same reaction proceeded more readily when the electrogenerated superoxide[13] was employed instead of KO_2 (Table I, method A). In the entries 7 and 8, the yields were low because of the production of the spiro-compounds formed by the treatment with base.[14]



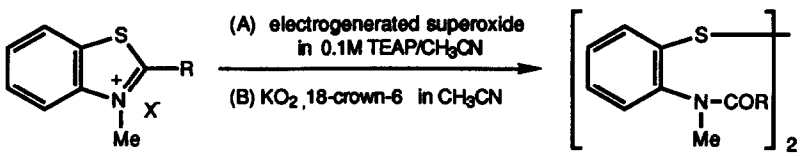
1 2 3

Scheme 1

Table I Reaction of 3-Methylbenzothiazolium Salts 1 with Superoxide

entry	substrate	R	X	E1/2 (V vs.SCE)	method	yield of 2	yield of 3
1	1a	H	I	-1.12	A	89%	3%
2	1b	NO_2	OSO_3Me	-0.76		95%	0
3	1c	OMe	I	-1.33		84%	7%
4	1d	Me	I	-1.30		87%	9%
5	1a	H	I	-1.12	B	71%	13%
6	1b	NO_2	OSO_3Me	-0.76		33%	41%
7	1c	OMe	I	-1.33		23%	19%
8	1d	Me	I	-1.30		11%	13%

When 1 was allowed to react with KOH instead of KO_2, the spiro-compound[14] was obtained exclusively, thus the reaction shown in Scheme 1 was suggested to be specific for superoxide. In order to verify whether C-2 proton abstraction was involved in the reaction process or not, 2-substituted 3-methylbenzothiazolium salts (1e-1h) were adopted as substrates, and the results showed that the absence of C-2 proton didn't affect the formation of 2, therefore superoxide was shown never to act as a simple base (Scheme 2 and Table II).



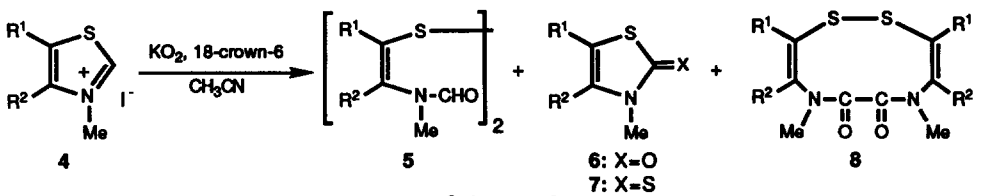
1e-1h Scheme 2 2e-2h

Table II Reaction of 2-Substituted 3-Methylbenzothiazolium Salts with Superoxide

entry	substrate	R	X	E1/2 (V vs.SCE)	method	yield (%)
1	1e	Ph	ClO_4	-1.08	A	74
2	1f	p-NO_2-Ph	OSO_3Me	-0.66		72
3	1g	p-MeO-Ph	ClO_4	-1.19		72
4	1h	Me	I	-1.51		41
5	1e	Ph	ClO_4	-1.08	B	81
6	1f	p-NO_2-Ph	OSO_3Me	-0.66		65
7	1g	p-MeO-Ph	ClO_4	-1.19		80
8	1h	Me	I	-1.51		23

In the case of **1h** as the substrate (entries 4 and 8), yields were low because the reduction potential of **1h** was relatively low to make the reaction slow, and the side-reaction couldn't be negligible.[15]

Next, the above reaction was applied to monocyclic thiazolium salts **4**. Dondoni *et al.* reported[16] that a few monocyclic thiazolium salts was subjected to the reaction with KO_2 in benzene or DMSO to afford low yield of 2-thiazolones **6** and their thio-analogues **7**, and that thiamine hydrochloride reacted with KO_2 to give analogous products.[17] We reinvestigated the reaction in detail and the disulfide **5** and novel 10 membered-ring compound **8** were revealed to be obtained other than the compounds **6** and **7** in acetonitrile (Scheme 3 and Table III). The structure of the compound **8** was confirmed by X-ray crystallographic analyses.[18] The reaction with electrogenerated superoxide afforded similar results except that the compound **7** was seldom obtained.[19]



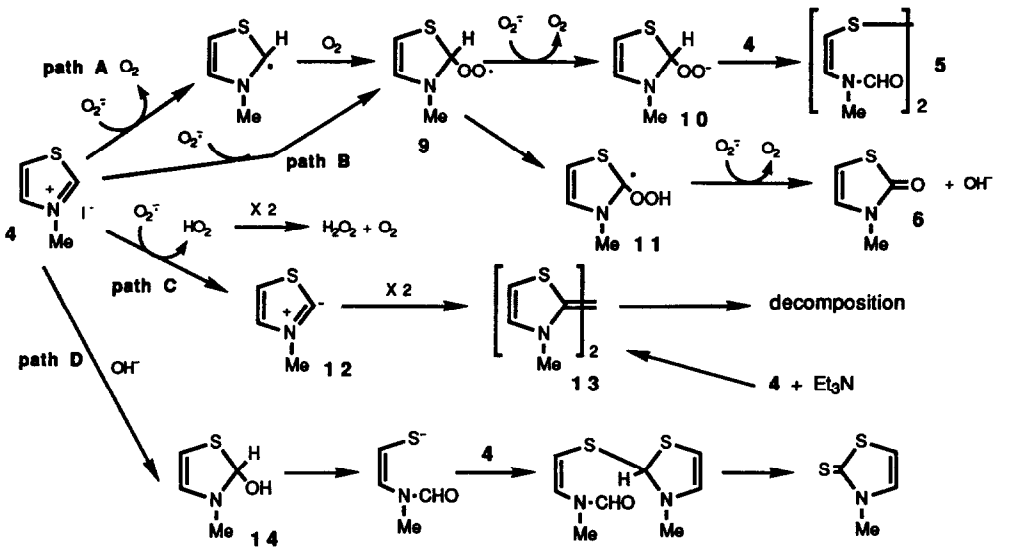
Scheme 3

Table III Reaction of 3-Methylthiazolium Salts **4** with Superoxide

entry	substrate	R^1	R^2	E1/2 (V vs. SCE)	yield (%) 5	6	7	8
1	**4a**	H	H	-1.54	26	14	16	0
2	**4b**	Me	Me	-1.60	39	13	24	3
3	**4c**	H	Me	-1.58	18	21	10	1
4	**4d**	Ph	H	-1.34	16	10	36	0

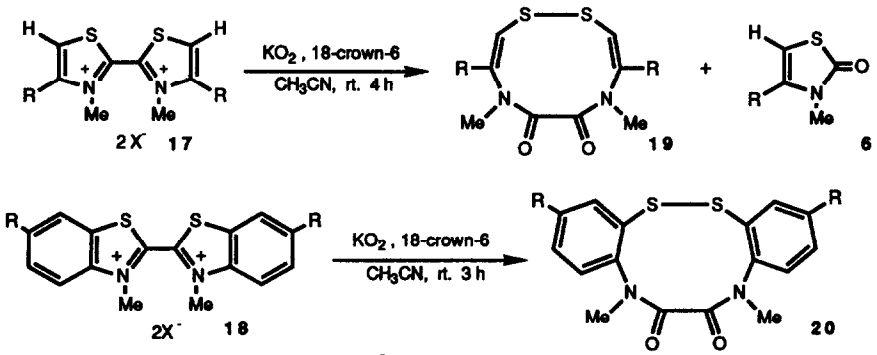
The reaction mechanism was thought as shown in Scheme 4. Benzothiazolium salts **1** have higher reduction potential than those of monocylic ones **4** and afforded disulfides **2** in good yields, and thus the formation of **2** or **5** may proceed through one electron transfer from superoxide to thiazolium salts **1** or **4** (Scheme 4, path A), although the direct nucleophilic attack of superoxide to **1** or **4** cannot be excluded because the use of oxygen atmosphere instead of argon afforded no effect on the reaction yields (path B). Peroxy radical **9** once formed might be reduced by another superoxide to give peroxy anion **10**, which might afford **5** by the reaction with **4**. When the radical **9** was isomerized to **11** before one-electron reduction, thiazolone **6** was obtained. In the case of monocyclic thiazolium salts, path A (or path B) supposed not to be dominant because of low reduction potential of them, thus path C or D might become preferable. Path C shows that superoxide acted as a base to abstract C-2 proton to form ylide intermediate **12**, which dimerized to **13**. The dimer **13** derived from monocyclic thiazolium salt is known to be quite unstable,[2d] hence it was probably decomposed in our reaction system, and the progress of path C might result in the low total yields in the case of **4** as a substrate. In fact, when **4** was treated with triethylamine under the condition according to the literature,[3] no products could be isolated. Thiazoline thione **7** was supposed to be formed by the attack of hydroxide ion which was produced accompanied by the formation of **6**, or existed in KO_2 as a contaminant. Thiazolium ion was attacked by hydroxide ion to give

alcohol **14**, followed by ring opening to form thiolate ion, which added to another **4** to afford **7** (path D). Although the formation mechanism of **8** was remained unclear, we were prompted to synthesize it by the fact that it was stable in the presence of superoxide.



Scheme 4

The mechanism shown in Scheme 4 suggested us that ten-membered ring compounds would be produced if the dimer of **4** whose C-2 position was bonded together was allowed to react through path A or path B. Thus 2,2'-bithiazoles **15**[20, 21] and 2,2'-bibenzothiazoles **16**[22] were synthesized according to the reported methods. They were treated with dimethyl sulfate to give bithiazolium salts **17** and **18**.[23] When **17** was subjected to the reaction with 3 eq. of KO_2 in the presence of 18-crown-6, 1,2,5,8-dithiadiazecine-6,7-dione **19** was obtained accompanied by 2-thiazolone **6**. The same reaction system was applied to bibenzothiazolium salts **18** to afford 11,14-dimethyldibenzo-[*c,l*][1,2,5,8]-dithiadiazecine-12,13-dione **20** (Scheme 5 and Table IV).

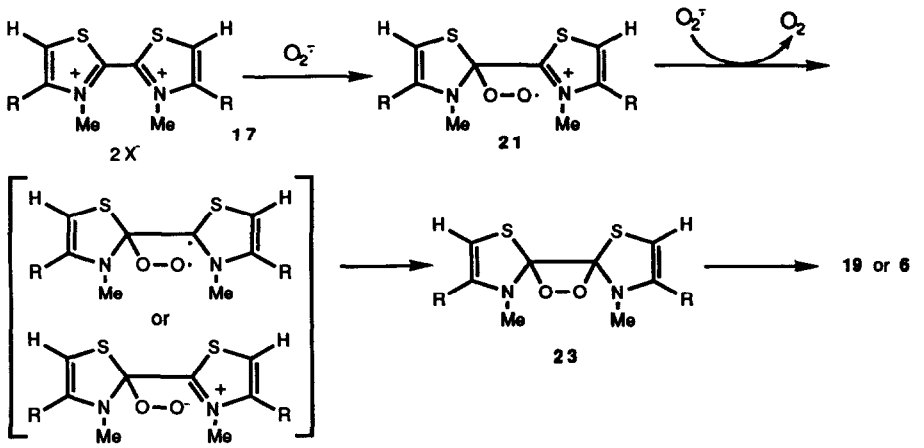


Scheme 5

Table IV Reaction of Bithiazolium Salts **17** and **18** with Superoxide

entry	substrate	R	X	products
1	**17a**	Me	OSO_3Me	**19a(=8c)**: 36%, **6c**: 22%
2	**17b**	Ph	ClO_4	**19b**: 38%, **6d**: 13%
3	**17c**	H	OSO_3Me	**19c**: 0%, **6a**: 2%[24]
4	**18a**	H	OSO_3Me	**20a**: 56%[25]
5	**18b**	Me	OSO_3Me	**20b**: 37%
6	**18c**	OMe	ClO_4	**20c**: 28%

The control experiments using KOH or KOH-H_2O_2 instead of KO_2 gave neither **19** nor **20** at all,[26] and thus the formation of dithiadiazecinedione was proved to be a specific reaction of superoxide. The formation mechanism of **19** and **20** was thought to be analogous to path B of Scheme 4. Path A didn't proceed in these cases because **17** and **18** showed completely reversible cyclic voltammogram even under oxygen atmosphere. It means that one-electron reduction species of **17** or **18** never react with molecular oxygen. Hence the first step was supposed to be nucleophilic addition of superoxide, followed by the one-electron reduction by another superoxide to form **22**, which might be cyclized to dioxetane type intermediate **23**. The compound **23** was supposed to be cleaved at O-O bond, and simultaneous S-S bond formation afforded **19**,[27] whereas normal dioxetane type cleavage gave **6** (Scheme 6).



Scheme 6

Additional but curious result was that electrogenerated superoxide hardly reacted with **17** or **18**, and the reaction was ended up with almost complete recovery of starting materials. It is of interest from the comparison with the data shown in Table I, which designated that electrogenerated superoxide gave better yields of **2** than KO_2. From these facts, we have indications that two different origins of superoxide exhibited different reactivity, namely, electrogenerated superoxide was superior to one electron reduction, while KO_2 was excellent in nucleophilic reaction. We have several other data that support the hypothesis,[28] although the reason for the alteration was remained unclear.

In this paper, we described the reaction of various thiazolium salts with superoxide. Thiazolium derivatives were revealed to have specific reactivity to superoxide to afford unique products which were synthesized only by this reaction system. To the best of our knowledge, there are few reports[8d] that claimed the formation of superoxide-specific products. Therefore, our reactions are promising method for the detection of superoxide in biological system, and the application is now under investigation.

ACKNOWLEDGMENT This work was supported in part by the Hoansha Foundation and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

EXPERIMENTAL

All melting points were taken on a Yanaco micro melting point apparatus and are uncorrected. The mass spectra were measured with JEOL JMS-D300 and JMS-SX102A instruments. IR spectra were recorded on Jasco A-102 Diffraction Grating Infrared Spectrophotometer. The nuclear magnetic resonance spectra were measured with JEOL JNM-FX100 and GX400 spectrometers using tetramethylsilane as an internal standard.

Reduction Potentials and Cyclic Voltammograms

The substrate (0.1 mmol) was dissolved in 10 ml of 0.1 M tetraethylammonium perchlorate solution of acetonitrile. Reduction potentials and cyclic voltammograms were recorded on a Yanaco P-1100 polarographic analyzer using glassy carbon as working, platinum as counter, and SCE as reference electrode, respectively.

General Procedure for the Reaction of 3-Methylbenzothiazolium Salts with Superoxide

Method A: The electrolysis was carried out with Yanaco VE-9 potentio/galvanostatic electrolyzer or Nikko Keisoku potentiogalvanostat NPGS-2501 using platinum electrode. The electric current was measured with Nikko Keisoku digital coulomb meter, NDCM-4. In the cathode chamber of H cell containing 0.1 M tetraethylammonium perchlorate solution of acetonitrile (40 ml), a stream of oxygen was bubbled through a gas dispersion tube, and the potential was set and maintained at -0.87 V vs. SCE until 33Q of electric current was cousumed. After argon bubbling instead of oxygen in the cathode chamber for 5 min, the compound 1 (0.15 mmol) was added and the mixture was allowed to stand at room temperature for 2h under argon atmosphere. Then the reaction solvent was evaporated and the residue was dissolved in ether to remove insoluble supporting electrolyte. The residual solution was evaporated, and the residue was chromatographed on alumina to give the products.

Method B: In the acetonitrile solution (40 ml) of the compound 1 (3.9 mmol), KO_2 (8.45 mmol) and 18-crown-6-ether (0.38 mmol) were added and the mixture was allowed to stand at room temperature for 2 h. Then ether was added to remove insoluble solid, and the filtered ether solution was evaporated off to leave the residue, which was chromatographed on alumina to give the products.

Bis[2-(*N*-formyl-*N*-methylamino)phenyl]disulfide (2a): This compound was obtained as a mixture of two confomational isomers, thus the major isomer was represented by A, and the minor one by B, respectively. Colorless needles from hexane-ether; mp 106-108°C. *Anal.* Calcd for $C_{16}H_{16}N_2O_2S_2$: C, 57.81; H, 4.85; N, 8.43. Found: C, 58.00; H, 5.07; N, 8.30. ^{1}H-NMR ($CDCl_3$) δ: A; 3.18 (s, 6H), 7.00-7.60 (m, 8H), 8.00 (s, 2H). B; 3.28 (s, 6H), 7.00-7.60 (m, 8H), 8.22 (s, 2H). ^{13}C-NMR ($CDCl_3$) δ: A; 33.43, 128.62, 128.91, 129.44, 129.72, 135.07, 140.43, 162.82. MS (*m/z*) 332 (M^+), 166 ($M^+/2$). IR (KBr) cm^{-1} 1680 (C=O).

Bis[2-(*N*-formyl-*N*-methylamino)-5-nitrophenyl]disulfide (2b): This compound was obtained as a mixture of conformational isomers. Yellow needles from hexane-ethyl acetate; mp 164°C (decomp.). *Anal.* Calcd for $C_{16}H_{14}N_4O_6S_2$: C, 45.49; H, 3.34; N, 13.26. Found: C, 45.68; H, 3.10; N, 13.34. ^{1}H-NMR ($CDCl_3$) δ: 3.28, 3.33, 3.40, 3.46 (s X 4, 6H), 7.20-7.40 (m, 6H), 8.00 (m, 2H). Methyl proton of N-Me group became single peak (δ; 3.35) when the measurement was carried out at 80°C in pyridine-d_6. ^{13}C-NMR ($CDCl_3$) for the major conformer δ: 33.24, 123.99, 127.77, 129.31, 136.09, 145.25, 147.83, 161.78. MS (*m/z*) 422 (M^+), 376 (M^+-NO_2). IR (KBr) cm^{-1} 1680 (C=O), 1525, 1350 (NO_2).

Bis[2-(*N*-formyl-*N*-methylamino)-5-methoxyphenyl]disulfide (2c): This compound was obtained as a mixture of two conformational isomers A and B. Pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: A; 3.19 (s, 6H), 3.78 (s, 6H), 6.65-7.18 (m, 6H), 8.07 (s, 2H). B; 3.28 (s, 6H), 3.72 (s, 6H), 6.65-7.18 (m, 6H), 8.20 (s, 2H). ^{13}C-NMR ($CDCl_3$) for the major conformer δ: 33.54, 55.66, 113.67, 113.80, 129.85, 132.69, 136.33, 160.12, 163.14. Exact MS *m/z* (M^+); Calcd for $C_{18}H_{20}N_2O_4S_2$: 392.086. Found: 392.088. IR (neat) cm^{-1} 1680 (C=O).

Bis[2-(*N*-formyl-*N*-methylamino)-5-methylphenyl]disulfide (2d): This compound was obtained as a mixture of two conformational isomers A and B. Colorless oil. ^{1}H-NMR ($CDCl_3$) δ: A; 2.36 (s, 6H), 3.17 (s, 6H), 6.92-7.52 (m, 6H), 8.03 (s, 2H). B; 2.34 (s, 6H), 3.30 (s, 6H), 6.92-7.52 (m, 6H), 8.24 (s, 2H). ^{13}C-NMR ($CDCl_3$) for the major conformer A δ: 21.14, 33.50, 128.31, 129.79, 130.60, 134.77, 138.08, 139.77, 162.93. Exact MS *m/z* (M^+); Calcd for $C_{18}H_{20}N_2O_2S_2$: 360.097. Found: 360.098. IR (neat) cm^{-1} 1680 (C=O).

The Reaction of 2-Substituted 3-Methylbenzothiazolium Salts (1e-1h) with Superoxide The same reaction system that was adopted for **1a-1d** was applied to **1e-1h**. Bis[*N*-benzoyl-*N*-methylamino)phenyl]disulfide **2e** was identified by the comparison of spectral and physical data with those of reported one.[29]

Bis[2-(*N*-4-nitrobenzoyl-*N*-methylamino)phenyl]disulfide (2f): Colorless needles from benzene; mp 188-189°C. *Anal.* Calcd for $C_{28}H_{22}N_4O_6S_2$: C, 58.55; H, 3.86; N, 9.76. Found: C, 58.48; H, 3.70; N, 9.49. ^{1}H-NMR ($CDCl_3$) δ: 3.44 (s, 6H), 6.88-7.20 (m, 8H), 7.40 (d, J=8.0Hz, 4H), 7.88 (d, J=8.0Hz, 4H). MS (*m/z*) 574 (M^+), 287 ($M^+/2$). IR (KBr) cm^{-1} 1640 (C=O), 1520, 1340 (NO_2).

Bis[2-(*N*-4-methoxybenzoyl-*N*-methylamino)phenyl]disulfide (2g): This compound was formed as a mixture of conformational isomers. The NMR data of the major one were shown below. Colorless granules from benzene; mp 146-147°C. *Anal.* Calcd for $C_{30}H_{28}N_2O_4S_2$: C, 66.15; H, 5.18; N, 5.14. Found: C, 65.90; H, 5.22; N, 5.25. ^{1}H-NMR ($CDCl_3$) δ: 3.39 (s, 6H), 3.76 (s, 6H), 6.65 (d, J=8.0Hz, 4H), 6.92-7.20 (m, 8H), 7.34 (d, J=8.0Hz, 4H). ^{13}C-NMR ($CDCl_3$) δ: 37.75, 55.17, 112.93, 126.98, 127.50, 127.94, 128.43, 128.93, 130.51, 134.13, 142.44, 160.82, 170.40. MS (*m/z*) 544 (M^+). IR (KBr) cm^{-1} 1640 (C=O).

Bis[2-(*N*-acetyl-*N*-methylamino)phenyl]disulfide (2h): This compound was obtained as a mixture of conformational isomers. The spectral data were shown concerning the major one. Colorless needles from benzene; mp 173-174°C. *Anal.* Calcd for $C_{18}H_{20}N_2O_2S_2$: C, 59.97; H, 5.59; N, 7.77. Found: C, 60.19; H, 5.58; N, 7.60. ^{1}H-NMR ($CDCl_3$) δ: 1.82 (s, 6H), 3.21 (s, 6H), 7.00-7.60 (m, 8H). ^{13}C-NMR ($CDCl_3$) δ: 22.03, 35.99, 127.14, 128.40, 128.65, 129.43, 135.21, 141.56, 170.76. MS (*m/z*) 360 (M^+), 180 ($M^+/2$). IR (KBr) cm^{-1} 1665 (C=O).

The Reaction of Monocyclic Thiazolium Salts 4 with Superoxide

To the acetonitrile solution (15 ml) of **4** (2.0 mmol), KO_2 (4.0 mmol) and 18-crown-6 (0.4 mmol) were added and the mixture was allowed to stand at room temperature for 30 min. Thereafter, ether was poured into the mixture to remove the insoluble salt, and the residual solution was evaporated off to leave the residue, which was chromatographed on alumina or silica gel to afford the products.

Bis[2-(*N*-formyl-*N*-methylamino)ethenyl]disulfide (5a): This compound was obtained as a mixture of conformational isomers. The NMR data was shown with respect to the major one. Pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 3.08 (s, 6H), 5.82 (d, J=13Hz, 2H), 7.03 (d, J=13Hz, 2H), 8.34 (bs, 2H). Exact MS *m/z* (M^+); Calcd for $C_8H_{12}N_2O_2S_2$: 232.034. Found: 232.034. FAB-MS [Pos.] *m/z* 233 $(M+H)^+$. FAB-MS [Neg.] *m/z* 231 $(M-H)^-$. IR (neat) cm^{-1} 1690 (C=O). 3-Methyl-2(3H)thiazolone (**6a**) and 3-methyl-2(3H) thiazoline thione (**7a**) were identified by the comparison of the spectral data with the reported compounds.[16]

Bis[2-(*N*-formyl-*N*-methylamino)-1,2-dimethylethenyl]disulfide (5b): This compound was obtained as a mixture of conformational isomers. The NMR data was shown with respect to the major one. Yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.94 (s, 6H), 2.09 (s, 6H), 2.94 (s, 6H), 7.90 (s, 2H). ^{13}C-NMR ($CDCl_3$) δ: 17.71, 18.43, 29.76, 130.29, 134.48, 162.33. Exact MS *m/z* ($M^+/2$); Calcd for $C_6H_{10}NOS$: 144.048. Found: 144.047. FAB-MS [Pos.] *m/z* 289 $(M+H)^+$. FAB-MS [Neg.] *m/z* 287 $(M-H)^-$. IR (neat) cm^{-1} 1665 (C=O).

3,4,5-Trimethyl-2(3H)thiazolone (6b): Colorless plates from hexane; mp 71°C. *Anal.* Calcd for C_6H_9NOS: C, 50.32; H, 6.33; N, 9.78; S, 22.39. Found: C, 50.54; H, 6.41; N, 9.71; S, 22.10. ^{1}H-NMR ($CDCl_3$) δ: 2.04 (s, 3H), 2.08 (s, 3H), 3.23 (s, 3H). ^{13}C-NMR ($CDCl_3$) δ: 11.51, 11.89, 29.67, 106.05, 126.70, 171.60. MS (*m/z*) 143 (M^+). IR (KBr) cm^{-1} 1650 (C=O).

3,4,5-Trimethyl-2(3H)thiazoline thione (7b): Pale yellow plates from ethanol; mp 103°C. *Anal.* Calcd for $C_6H_9NS_2$: C, 45.28; H, 5.70; N, 8.80. Found: C, 45.44; H, 5.75; N, 8.78. ^{1}H-NMR ($CDCl_3$) δ: 2.16 (s, 3H), 2.18 (s, 3H), 3.66 (s, 3H). ^{13}C-NMR ($CDCl_3$) δ: 11.54, 12.93, 34.84, 117.31, 134.48, 185.62.MS (*m/z*) 159 (M^+). IR (KBr) cm^{-1} 1120 (C=S).

3,4,5,8,9,10-Hexamethyl-1,2,5,8-thiadiazecine-6,7(5H,8H)dione (8b): Colorless prisms from ethanol; mp 158°C. *Anal.* Calcd for $C_{12}H_{18}N_2O_2S_2$: C, 50.32; H, 6.34; N, 9.78; S, 22.39. Found: C, 50.31; H, 6.38; N, 9.72; S, 22.12. ^{1}H-NMR ($CDCl_3$) δ: 2.08 (s, 12H), 2.99 (s, 6H). ^{13}C-NMR ($CDCl_3$) δ: 18.59, 22.89, 32.46, 132.90, 144.84, 164.24. MS (*m/z*) 286 (M^+). IR (KBr) cm^{-1} 1640 (C=O). Final structural elucidation of **8b** was carried out by X-ray crystallographic analysis.[18]

Bis[2-(*N*-formyl-*N*-methylamino)-2-methylethenyl]disulfide (5c): This compound was obtained as a mixture of conformational isomers. The NMR data were shown with respect to the major one. Yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 2.00 (d, J=0.5Hz, 6H), 2.98 (s, 6H), 5.92 (d, J=0.5Hz, 2H), 7.92 (s, 2H). ^{13}C-NMR ($CDCl_3$) δ: 20.76, 30.89, 120.91, 139.07, 161.87. Exact MS *m/z* (M^+/2); Calcd for C_5H_8NOS: 130.033. Found: 130.035. FAB-MS [Pos.] *m/z* 261 $(M+H)^+$. FAB-MS [Neg.] *m/z* 259 $(M-H)^-$. IR (neat) cm^{-1} 1670 (C=O).

3,4-Dimethyl-2(3H)thiazolone (6c): Colorless plates from ether-hexane; mp 47°C. *Anal.* Calcd for C_5H_7NOS: C, 46.49; H, 5.46; N, 10.84; S, 22.39. Found: C, 46.38; H, 5.40; N, 10.62; S, 22.10. ^{1}H-NMR ($CDCl_3$) δ: 2.12 (d, J=0.5Hz, 3H), 3.24 (s, 3H), 5.70 (d, J=0.5Hz, 1H). MS (*m/z*) 129 (M^+). IR (KBr) cm^{-1} 1640 (C=O).

3,4-Dimethyl-2(3H)thiazoline thione (7c): Colorless needles from ethanol; mp 112°C. *Anal.* Calcd for $C_5H_7NS_2$: C, 41.38; H, 4.86; N, 9.65. Found: C, 41.42; H, 4.85; N, 9.56. ^{1}H-NMR ($CDCl_3$) δ: 2.12 (d, J=0.5Hz, 3H), 3.24 (s, 3H), 5.70 (d, J=0.5Hz, 1H). MS (*m/z*) 145 (M^+). IR (KBr) cm^{-1} 1100 (C=S).

4,5,8,9,-Tetramethyl-1,2,5,8-thiadiazecine-6,7(5H,8H)dione (8c): Colorless needles from isopropanol; mp 197-198°C. *Anal.* Calcd for $C_{10}H_{14}N_2O_2S_2$: C, 46.49; H, 5.46; N, 10.84. Found: C, 46.19; H, 5.42; N, 10.64. ^{1}H-NMR ($CDCl_3$) δ: 2.09 (d, J=0.5Hz, 6H), 3.00 (s, 6H), 6.35 (q, J=0.5Hz, 2H). ^{13}C-NMR ($CDCl_3$) δ: 21.20, 32.64, 122.85, 153.49, 163.96. MS (*m/z*) 258 (M^+). IR (KBr) cm^{-1} 1640 (C=O).

Bis[2-(*N*-formyl-*N*-methylamino)-1-phenylethenyl]disulfide (5d): This compound was obtained as a mixture of conformational isomers. The NMR data was shown with respect to the major one. Yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 2.93 (s, 6H), 6.44 (s, 2H), 7.32-7.45 (m, 10H), 8.13 (s, 2H). Exact MS *m/z* (M^+/2); Calcd for $C_{10}H_9NOS$: 192.048. Found: 192.046. FAB-MS [Pos.] *m/z* 385 $(M+H)^+$. FAB-MS [Neg.] *m/z* 383 $(M-H)^-$. IR (neat) cm^{-1} 1680 (C=O).

3-Methyl-4-phenyl-2(3H)thiazolone (6d): Colorless plates from hexane-dichloromethane; mp 123°C. *Anal.* Calcd for $C_{10}H_9NOS$: C, 62.80; H, 4.74; N, 7.32. Found: C, 62.62; H, 4.65; N, 7.38. ^{1}H-NMR ($CDCl_3$) δ: 3.39 (s, 3H), 6.80 (s, 1H), 7.32-7.39 (m, 5H). MS (*m/z*) 191 (M^+). IR (KBr) cm^{-1} 1660 (C=O).

3-Methyl-5-phenyl-2(3H)thiazoline thione (7d): Pale yellow needles from ethanol; mp 159°C. *Anal.* Calcd for $C_{10}H_9NS_2$: C, 57.97; H, 4.38; N, 6.76. Found: C, 58.01; H, 4.42; N, 6.71. ^{1}H-NMR ($CDCl_3$) δ: 3.74 (s, 3H), 7.23 (s, 1H), 7.31-7.41 (m, 5H). MS (*m/z*) 207 (M^+). IR (KBr) cm^{-1} 1130 (C=S).

The Reaction of Bithiazolium Salts 17 and 18 with Superoxide

To the acetonitrile solution (40 ml) of **17** or **18** (1.0 mmol), KO_2 (3.0 mmol) and 18-crown-6 (1.0 mmol) were added and the mixture was allowed to stand at room temperature for 4h. Then ether was added and the mixture was filtered to remove insoluble salt. The filtrate was evaporated off to leave the residue, which was chromatographed on alumina to give the products.

5,8-Dimethyl-4,9-diphenyl-1,2,5,8-dithiadiazecine-6,7(5H,8H)-dione (19b): This compound was obtained as a mixture of two conformational isomers A (major) and B (minor). Pale yellow prisms from ether-ethyl acetate; mp 181-182°C. *Anal.* Calcd for $C_{20}H_{18}N_2O_2S_2$: C, 62.80; H, 4.74; N, 7.32. Found: C, 62.66; H, 4.65; N, 7.36. ^{1}H-NMR ($CDCl_3$) δ: A; 2.98 (s, 6H), 6.96 (s, 2H), 7.24-7.60 (m, 10H). B; 2.88 (s, 6H), 6.00 (s, 2H), 7.24-7.60 (m, 10H). ^{13}C-NMR ($CDCl_3$) δ: A; 34.32, 119.94, 128.40, 128.78, 130.70, 133.71, 155.32, 164.99. B; 34.09, 115.89, 126.92, 128.88, 129.11, 137.32, 140.95, 162.94. MS (*m/z*) 382 (M^+). IR (KBr) cm^{-1} 1660 (C=O).

11,14-Dimethyldibenzo[*c,f*][1,2,5,8]dithiadiazecine-12,13(11H,14H)-dione (20a): This compound was reported in a communication,[30] but no structural elucidation was carried out. Pale yellow granules from ethyl acetate; mp 207-208°C. *Anal.* Calcd for $C_{16}H_{14}N_2O_2S_2$: C, 58.16; H, 4.27; N, 8.48. Found: C, 58.13; H, 4.17; N, 8.49. ^{1}H-NMR ($CDCl_3$) δ: 3.04 (s, 6H), 7.20-7.68 (m, 8H). ^{13}C-NMR ($CDCl_3$) δ: 36.51(36.54), 129.84, 131.80, 132.14, 136.28, 138.17, 144.43, 163.64. MS (*m/z*) 330 (M^+),165 (M^+/2). IR (KBr) cm^{-1} 1645 (C=O).

3,8,11,14-Tetramethyldibenzo[*c,f*][1,2,5,8]dithiadiazecine-12,13(11H,14H)-dione (20b): Colorless granules from ether; mp 230-231°C. *Anal.* Calcd for $C_{18}H_{18}N_2O_2S_2$: C, 60.31; H, 5.06; N, 7.82. Found: C, 60.15; H, 5.23; N, 7.58. ^{1}H-NMR ($CDCl_3$) δ: 2.38 (s, 6H), 3.02 (s, 6H), 7.16-7.42 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 20.91, 36.60, 131.68, 132.57, 135.76, 138.52, 140.10, 141.63, 163.84. MS (*m/z*) 358 (M^+),179 (M^+/2). IR (KBr) cm^{-1} 1640 (C=O).

3,8-Dimethoxy-11,14-dimethyldibenzo[*c,f*][1,2,5,8]dithiadiazecine-11,12(11H, 14H)-dione (20c): Pale yellow prisms from ethyl acetate; mp 203-204°C. *Anal.* Calcd for $C_{18}H_{18}N_2O_4S_2$: C,55.37; H, 4.65; N, 7.18. Found: C, 55.21; H, 4.52; N, 7.05. ^{1}H-NMR ($CDCl_3$) δ: 3.02 (s, 6H), 3.85 (s, 6H), 7.01 (dd, J=2.9, 8.8Hz, 2H), 7.20 (d, J=2.9Hz, 2H), 7.42 (d, J=8.8Hz, 2H).

^{13}C-NMR ($CDCl_3$) δ: 36.67, 55.67, 117.45, 122.17, 132.96, 136.76, 137.02, 159.51, 164.19. MS (*m/z*) 390 (M^+),195 ($M^+/2$). IR (KBr) cm^{-1} 1640 (C=O).

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23. Since it was difficult to crystallize the compounds **17b** and **18c** as methosulfate salts, they were treated with $NaClO_4$ to afford corresponding perchlorate salts.

24. The compound **17c** was almost insoluble in acetonitrile, and the starting material was recovered even after 7h's reaction.

25. In the case of bibenzothiazolium salts as substrates, the spiro-compounds reported in ref.14 were obtained in 30%(from **18a**), 39%(from **18b**), and 21%(from **18c**), respectively.

26. Control experiments afforded the compounds **6** from **17**, spiro-compounds[14] from **18**, respectively.

27. Similar rearrangement of dioxetane to large membered ring instead of diketone was observed in the reaction of 2-(1,3-dithia-2-cyclohexylidenyl)-1,3-dithiane with singlet oxygen. See, Adam, W.; Liu, J-C. *J. Am. Chem. Soc.*, **1972**, *94*, 1206.

28. The alteration of the reactivity was also observed in the reaction of halotriazines with superoxide, and it was reported in ref. 5c. The other observation was performed when superoxide was allowed to react with quaternary salts of heteroaromatics which have ester group as a substituent. In the reaction, potassium superoxide preferred to attack ester group, whereas electrogenerated superoxide afforded the products which were derived from one-electron reduction of the starting materials. The effects of solvent and counter cation on the reaction of superoxide will be reported elsewhere.

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