# Tri(hetero)substituted Carbonium Ions. VII.[1] Effect of the Ring System on the Ambident Reactivity of Cyclic Dithiocarbamidium Ions[2]

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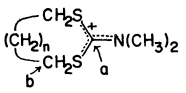
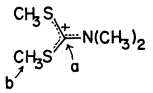
In order to study the effect of structure on the ambident reactivity of cyclic dithiocarbamidium ions, two *endo*-iminium type cations, 2-methylthio-3-methyl-4,5-dihydrothiazolium ion (**5**) and 2,3,5,6-tetrahydrothiazolo-[2,3-*b*]-thiazolium ion (**6**) were prepared. Their electrophilic reactivities were studied and compared with those of the *exo*-iminium type cations, 2-dimethylamino-1,3-dithiolan-2-ylium ion (**1**) and its ring analogues. 3-Dimethylamino-2,4-benzodithiepan-3-ylium ion (**7**) was prepared and its ambident reactivity was studied. Examination of the products obtained from their reactions with various nucleophiles revealed that the three cation have two reactive sites, *i.e.*, the central ($sp^2$) carbon (site *a*) and the *S*-methylene (or *S*-methyl) ($sp^3$) carbon atoms (site *b*). Significant differences in the electrophilic behavior of the *endo*- and *exo*-iminium type cations were observed. They were discussed in terms of the structures as estimated from the spectra. Kinetic experiments showed that the reactivities at site *a* of these cations with hydroxide ion, relative to that of **1**, are 22.5 (**5**): 16.6 (**6**): 27.2 (**7**), and at site *b* with *N,N*-dimethyldithiocarbamate ion are 3.3 : 282 : $>10^4$. The reactivity order suggests that the reactivities at the two sites, especially at site *b*, are very sensitive to a change in the ring system of the cations.

In previous papers of this series,[3–6] the electrophilic behaviors of various dithiocarbamidium ions[7] including 2-dimethylamino-1,3-dithiolan-2-ylium ion (**1**), its ring analogues (**2** and **3**), and an open-chain analogue (**4**) were reported. It was shown that (a) the carbonium ions have two reactive sites, *a* and *b* in the formula shown below, (b) the reaction course is determined by both the nature of the attacking reagent employed and the structure of the cation and (c) the electrophilic reactivities at both sites depend markedly upon the the ring-size of the cation.

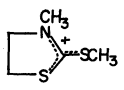


**1**: $n=0$
**2**: $n=1$
**3**: $n=2$

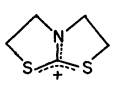


**4**

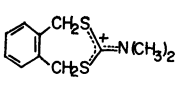
In order to obtain further information on the relationship between the structure and reactivity of dithiocarbamidium ions, the electrophilic behavior of 2-methylthio-3-methyl-4,5-dihydrothiazolium ion (**5**) and 2,3,5,6-tetrahydrothiazolo[2.3-*b*]thiazolium ion (**6**) has been investigated and compared with that of cation **1** having the same ring-size as **5** (and **6**). While the cyclic cations such as **1** and **2** are tentatively classified as *exo*-iminium type, **5** and **6** can be classified as *endo*-iminium type. The electrophilic reactivity of another *exo*-iminium type cation, 3-dimethylamino-2,4-benzodithiepan-3-ylium ion (**7**), was studied and compared with that of monocyclic **3** having the same ring-size as **7**.



**5**



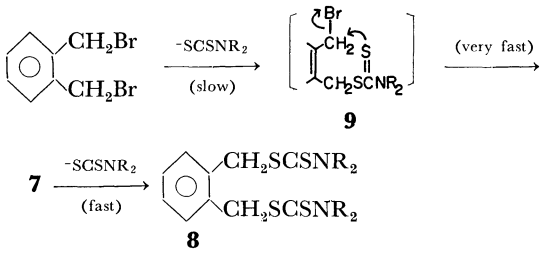
**6**



**7**

## Results

*Preparation of Carbonium Salts.* Cations **5** and **6** were obtained as the iodide (**5a**)[8] and the chloride (**6a**)[9] by the methods in literature. Perchlorate (**5b**) was prepared by methylation of 3-methylthiazolidine-2-thione with dimethyl sulfate followed by treatment with sodium perchlorate. Treatment of **6a** with sodium perchlorate gave perchlorate (**6b**). Cation **7** was obtained as perchlorate by the reaction of *o*-xylylene dibromide with sodium *N,N*-dimethyldithiocarbamate followed by treatment with sodium perchlorate. Even under equimolar conditions, the disubstituted product, *o*-xylylene bis(dithiocarbamate) (**8**), was formed in considerable yields together with **7** and the product ratio varied with the solvent used. This suggests that, as in the reactions of 1,2-dichloroethane and 1,3-dichloropropane with the dithiocarbamate anion,[3,5,10] neighboring-group participation of the dithiocarbamate function accelerates the second substitution process, **9**→**8**, through the intermediacy of the isolated anchimeric cation (**7**), as illustrated below.



All carbonium salts thus obtained were identified by means of NMR spectroscopy and elemental analyses. The spectral data for the cations are given in Table 1 together with those for **1** and **3** as references.

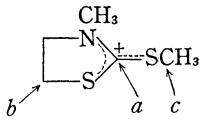
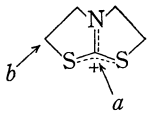
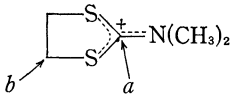
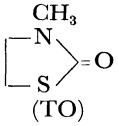
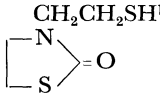
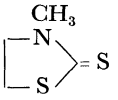
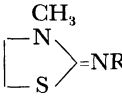
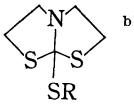
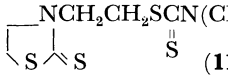
*Reactions with Various Nucleophiles.* In order to demonstrate the ambident character of the cations, the reactions of **5** and **6** with a variety of nucleophiles were studied. The products thus obtained are given in Table 2. They were identified by IR, NMR and UV spectroscopy and/or comparison of their physical properties with those of authentic samples (see Experimental). All the products except for **10**, **11**, and the 2-imino-thiazolidines are known compounds,

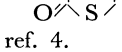
Table 1. Melting points and spectral data of the carbonium salts

| Cation | Mp, °C (counter anion) | UV[a] $\lambda_{max}$, mμ | NMR,[b] δ ppm -$SCH_2$- | -$NCH_2$- | Others |
|---|---|---|---|---|---|
| **5** | 132—135 ($I^-$)[c] d) ($ClO_4^-$) | 252 | 3.82(t) | 4.55(t) | $NCH_3$ 3.55(s) $SCH_3$ 2.94(s) |
| **6** | 93—95 ($Cl^-$)[e] 158—159 ($ClO_4^-$) | 257 | 4.18(s)[f] | | |
| **1**[g] | | 249 | 3.61(s) | | $NCH_3$ 4.08(s) |
| **7** | 205—207 ($ClO_4^-$) | 267 | 5.10(s) | | $NCH_3$ 2.95—3.10(m) Aromatic 7.7—7.9(m) |
| **3**[h] | | 275 | 3.47 | | $NCH_3$ 3.61(s) |

a) In water; the molar extinction coefficients (ε) were about $10^4$ for all carbonium salts. b) In $(CD_3)_2SO$; multiplicity: s=singlet, t=triplet, and m=multiplet. c) Reported mp 132—135°C: ref. 8. d) The perchlorate was so hygroscopic that mp could not be measured. e) Reported mp 95°C: ref. 9. f) In $D_2O$: ref. 9. g) Taken from ref. 3. h) Taken from ref. 5.

Table 2. Reactions of the cations with nucleophiles

| Nucleophile |  (5) Product (Attacking site) |  (6) Product (Attacking site) |  (1) (Attacking site) |
|---|---|---|---|
| -OH |  (TO) (*a*) |  ($CH_2CH_2SH$[b]) (*a*) | (*a*) |
| $-OCH_3$ | TO (*a*) | | (*a*) |
| -CN |  (TS) (*c*) |  (**10**) (*a*) | (*a*) |
| $H_2NR$ |  (*a*) | | (*a*) |
| -SR | |  b)d) (*a*) | (*b*) |
| $-SCSN(CH_3)_2$ | TS + $CH_3SCN(CH_3)$ (*c*) |  (**11**) (*b*) | (*b*) |
| $N(C_2H_5)_3$ | TS + $[CH_3\overset{+}{N}Et_3]$ (*c*) | An unidentified product[e] | f) |

a) Ref. 4. b) Ref. 9. c) R=phenyl and $NHSO_2C_6H_4CH_3(p)$. d) R=$CH_2CH_2N$  e) In very poor yield; bp 86—89°C/0.3 mmHg. f) A proton abstraction reaction was observed: ref. 4.

The NMR spectrum of **10** showed only one slightly split singlet signal at δ 3.77 (Fig. 1) and the IR spectrum an absorption band at 2200 $cm^{-1}$ due to the cyano group. The NMR spectrum of **11**, on the other hand, showed several signals which were assigned as shown in Fig. 1 through comparison with spectra of 3-methylthiazolidine-2-thione and methyl *N,N*-dimethyldithiocarbamate. The structure of **11** was further confirmed by the identity of its UV spectrum with that of an equimolar mixture of the two references.

It was found that **7** reacted with hydroxide and *N,N*-dimethyldithiocarbamate ions to yield *o*-mercaptomethylbenzyl thiolcarbamate (**12**) and the bis(dithiocarbamate) (**8**), respectively. The formation of **12** and **8** is best explained as a result of the attack of the nucleophile on the central carbon and on the *S*-methylene carbon, respectively.

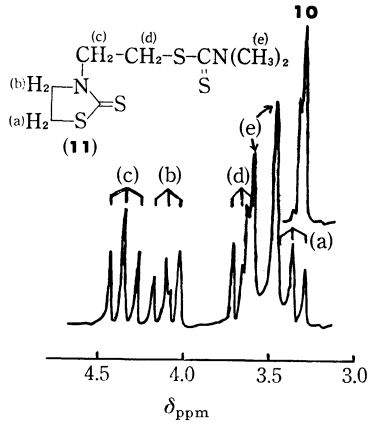
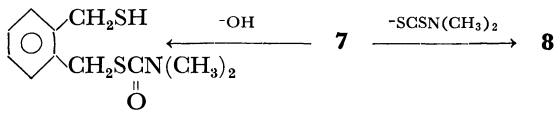



Fig. 1. NMR spectra of **10** and **11** ($CDCl_3$).




**12**

*Kinetic Studies.* The reaction at site *a* is kinetically controlled (mode A) whereas the reaction at site *b* or *c* is thermodynamically controlled (mode B).[3,4] In order to estimate the reactivity of modes A and B of the cation, the rates of reactions of the carbonium perchlorates with hydroxide and *N*,*N*-dimethyldithiocarbamate ions were measured, according to the procedures previously reported.[5]

The reaction of the cation with hydroxide ion was carried out in buffer solutions at 30 °C under pseudo-first-order conditions. Plots of the observed pseudo-first-order rate constants ($k_{obs}$) against the hydroxide concentrations were linear in the pH ranges studied for the cations (Fig. 2). The values of the second-order rate constants ($k_a$) for the reactions with hydroxide ion were obtained from the slopes of the straight lines obtained. The reaction of the cation with the dithiocarbamate ion was studied in dimethylformamide (DMF) at 30 °C. The values of the second-order rate constants ($k_b$) for the reaction with the dithiocarbamate ion were obtained from the slopes of the second-order rate plots (Fig. 3). The reaction of **7** with the anion

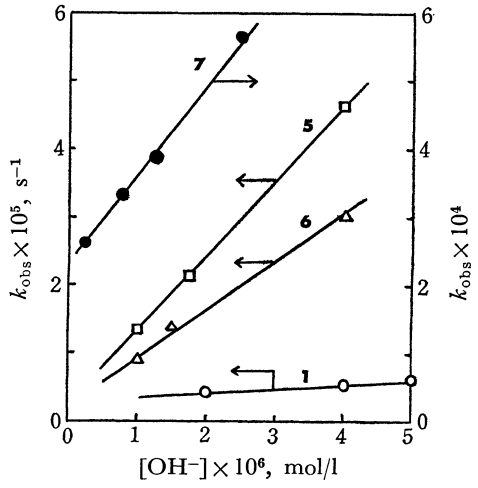



Fig. 2. Plots of $k_{obs}$ *vs.* [$OH^-$]

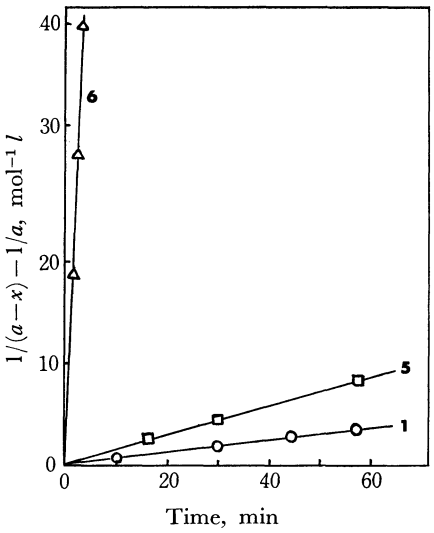



Fig. 3. Second-order rate plots for the reaction of the dithiocarbamate ion.

TABLE 3. RELATIVE REACTIVITIES OF MODE A AND B FOR THE CARBONIUM IONS (30°C)

| Cation | Mode A Rel. $k_a$ | Mode B[a] Rel. $k_b$ |
|---|---|---|
| **1**[b] | 1.0[c] | 1.0[d] |
| **5** | 22.5 | 3.3[e] |
| **6** | 17.6 | 282 |
| **7** | 27.2 | Very fast ($>10^4$)[f] |
| **3** | 32.5 | 23.8 |

a) Unless otherwise stated, the reaction proceeded at site *b*. b) Ref. 5. c) $k_a = 5.1 \times 10^{-1}\,M^{-1}s^{-1}$. d) $k_b = 1.30 \times 10^{-3}\,M^{-1}s^{-1}$. e) At site *c*. f) See text.

was too fast to be measured by the present method. The value of $k_b$ for **7** was found to be at least 10 $M^{-1}$ $s^{-1}$. Table 3 shows the relative values of $k_a$ and $k_b$ for the cations.

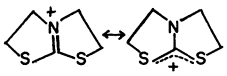
## Discussion

*Spectra and Relative Stabilities of the Carbonium Ions.* The extent of stabilization of tri(hetero)carbonium ions depends upon the electron-donating power of the hetero-substituents directly adjoining the electron-deficient carbon atom. However, for the series of cyclic dithiocarbamidium ions we studied the extent of stabilization is expected to depend upon other structural factors, *e.g.*, the ring-size and the ring system, which enhance or diminish the internal dissipation of the positive charge.

On the other hand, it has been established[11] that the relative stability of a series of open-chain tri(hetero)-carbonium ions is linearly correlated with the transition energy ($1/\lambda_{max}$) in the electronic spectra; *the more stabilized the tri(hetero)carbonium ion, the shorter (higher energies) the wavelengths to which the maximum absorption band ($\lambda_{max}$) shifts.*[12] The linear correlation has not only been confirmed by simple HMO calculation[11] but also accepted experimentally for a series of cyclic dithiocarbamidium ions of *exo*-iminium type,[5,13]

Thus, the UV spectral data (Table 1) indicate that the stability of **5** (*endo*-iminium) is comparable to that of **1** (*exo*-iminium) and that both cations are more stabilized than open-chain **4** ($\lambda_{max}$ 276 m$\mu$[5]) presumably due to the more developed 1,3-overlapping in the ring system. The former is of particular interest since it could be expected that **5** is more stabilized than **1** if the formal ring-closures leading to the *endo*- (**5**) and *exo*-iminium type (**1**) increase the conjugative (stabilizing) effect of a combination of the nitrogen and sulfur atoms and of the two sulfur atoms in each ring *by the same factor*.[14] This would imply that participation of the nonbonding electron pair on the nitrogen in **5** is less fully involved in the 1,3-overlap seemingly due to twisting of the axis of symmetry of the nitrogen p orbital out of parallel with that of the vacant p$\pi$ orbital of the $sp^2$ carbon.

Another interesting fact obtained from UV spectral comparison is that bicyclic **6** is less stable than **1** and **5**. This suggests that the contribution to stabilization from the iminium structure (**6'**) is to a greater extent reduced by steric requirement presumably due to a larger twisting of the nitrogen p orbital described above, thus making the contribution from the sulfonium structure (**6''**) relatively more favored.[15] This is supported by the unusual observation that the NMR spectrum of **6** showed only singlet at $\delta$ 4.18, indicating that the *N*-methylene protons of **6** are more shielded than those of **5** ($\delta$ 4.55) while the *S*-methylene protons of **6** ($\delta$ 4.18) are much more deshielded than those of **5** ($\delta$ 3.82) and **1** ($\delta$ 3.61). The spectral observation also indicates a structure with all eight skeletal atoms nearly in one plane for **6**.[15]



**6'** **6''**

Comparison of $\lambda_{max}$ between the two seven-membered cations shows that **7** is more stabilized than **3**; this suggests that the seven-membered ring of **7** is undoubtedly constrained to a near-planar configuration by the fused benzene ring, so that the 1,3-overlap in **7** is more effective.

It can be said that the stabilities of the cyclic dithiocarbamidium ions depend markedly not only on the ring-size but also on the ring system, and decrease in the order: **1**≈**5**>**6**>**2**>**7**>**3**≈**4**.

*Effect of Ring System on the Ambident Reactivity*

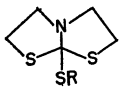
The stability of the tri(hetero)carbonium ion plays an important role in determining both the reaction course and the dual reactivities at the two sites.[4,5]

Let us discuss the effect of the ring system on the course of reaction of the cations with nucleophiles. An examination of the structures of the products given in Table 2 shows that the cations have two electrophilic sites and that the course of reaction with nucleophiles follows the selectivity rule[4]; hard bases, *e.g.*, $OH^-$, react at site *a* (mode A) while soft bases, *e.g.*, $R_2NCSS^-$, and bulky bases react at site *b* or *c* (mode B). However, the following significant differences in the reaction course of the *endo*- and *exo*-iminium types were observed: (a) the *endo*-iminium **5** directs the attack of $CN^-$ to site *c* (mode B) while the *exo*-iminium **1** (and **6**) directs it to site *a* (mode A); (b) the bicyclic *endo*-iminium **6** directs the attack of $RS^-$ to site *a* while **1** directs it to site *b*.

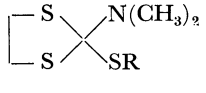
Case (a) is not well understood at the present stage. A possible factor responsible for the difference might be steric hindrance by the *N*-methyl of **5** arising from twisting of the nitrogen to attack $CN^-$ at site *a*.

Case (b), on the other hand, is essentially the same as in the course of reaction with $RS^-$ observed between **1** and open-chain **4** which has been best explained in terms of the difference in stability between **1** and **4**.[6] Thus, a similar argument is possible.

The major factor deciding the reaction course is the energy gap between the cation and its kinetically controlled (mode A) product.[4,16] In view of the fact that **6** is less stable than **1**, the energy gap between **6** and its mode A product (**13**) might be larger than that between **1** and its mode A product (**14**) since the process from **6** to **13** would result in the release of energy of both charge neutralization and twisting (ring strain) while the process from **1** to **14** would result in the release of only charge neutralization. As



**13**



**14**

a result, the position of the equilibrium in Eq. 1 shifts to the right leading to the formation of the kinetic adduct (**13**), whereas that in Eq. (2) shifts to the left leading to the formation of the thermodynamically stable product (**15**) *via* mode B.

$$\mathbf{6} + RS^- \rightleftharpoons \mathbf{13} \quad (1)$$

$$\mathbf{15} \longleftarrow \mathbf{1} + RS^- \rightleftharpoons \mathbf{14} \quad (2)$$

**15**

Let us now discuss the effect of ring system on the reactivities of both modes of the cations on the basis of the kinetic data given in Table 3. Figure 4 shows plots of the relative reactivities of mode B against those of mode A for the cations of *endo*- and *exo*-iminium types.

It has been suggested[5,16] that the reactivity of modes A and B depends, respectively, upon the energy gap between the cation and the kinetic adduct (the carbinol in this case) and between the cation and the transition state. If the energy contents of the carbinols for mode A and of the transition states for mode B were nearly constant, irrespective of changes in structures of the cations, that is, the rates of reactions were determined solely or at least favorably by the stability of the cations themselves, the rates of reactions of both modes would increase with a decrease in stability of the cation. This is the case for a series of the cations of *exo*-iminium type (Fig. 4). Thus, in view of the stability order of the cations, a similar argument is possible in explaining the observation qualitatively that

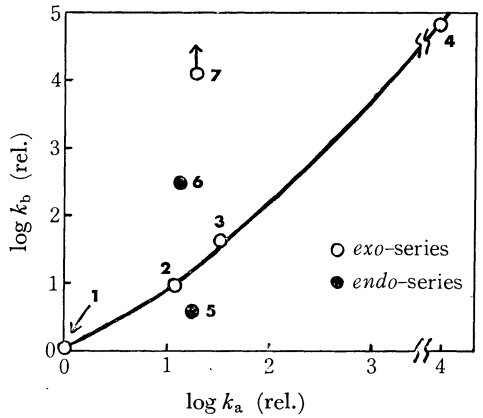



Fig. 4. Plots of log $k_b$ *vs.* log $k_a$.

the $k_a$-value for **6** is larger than that for **1** and that the $k_a$-value for **7** is smaller than that for **3**.

It is obvious, however, that the stability order cannot account for the following observations; (a) mode A reactivity of **5** is larger than that of **1**, (b) mode B reactivity of **6** is much higher than not only that of **1**, but that of the six-membered **2** although **2** is less stable than **6**, and (c) mode B reactivity of **7** is much larger than that of **3** even though **7** is more stable than **3**. Thus, we should consider the unusual observations which are connected purely with the effect of ring system on the reactivity.

Observation (a) cannot be explained at the present stage. The higher reactivity of mode B of **6**, compared with that of the less stable cation **2**, indicates that **6** should represent the transition state of lower energy, *i.e.*, $\Delta F_B^{\neq}$ for **6**$<\Delta F_B^{\neq}$ for **2** in the schematic energy profile (Fig. 5). In view of the structural aspects for **6** it seems that the following factors are operative in activating the reaction center (site *b*); a more favorable contribution to stabilization from the sulfonium structure (**6″**) by steric requirement and a relief of the ring strain. Similarly, the higher reactivity of **7** indicates that $\Delta F_B^{\neq}$ for **7** is smaller than that for **3** in the energy profile even though the energy level for **7** is lower than that for **3**. It appears that the enhanced reactivity of **7** can be ascribed to two factors; the constrained near-planar configuration and the electronic effect of the fused benzene nucleus on the benzylic carbon atom.

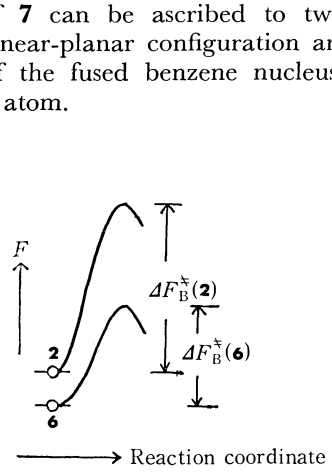



Fig. 5. Schematic energy profiles for mode B.

## Experimental

*General.* Melting and boiling points are uncorrected. IR and UV spectra were recorded with Hitachi EPI-S2 and EPS-2 spectrometers. NMR spectra were obtained with a Japan Electron Optics C-100 spectrometer. Chemical shifts are reported in terms of $\delta$ ppm downfield from tetramethylsilane as an internal standard.

*Materials.* 3-Methylthiazolidine-2-thione was obtained in 65% yield from *N*-methylethanol amine and carbon disulfide by a modification of the method reported previously.[8] Bis(*β*-chloroethyl)amine hydrochloride and *o*-xylylene dibromide were prepared according to the procedure in literature.[9,17] Commercial reagents and solvents were used after purification by standard methods.

*2-Methylthio-3-methyl-4,5-dihydrothiazolium Salts (**5**).* 3-Methylthiazolidine-2-thione (7.5 g) was dissolved in 6.3 ml of methyl iodide. The mixture was heated at 40 °C for 30 min giving precipitates of the carbonium iodide (**5a**) quantitatively. Recrystallization of the precipitates from ethanol gave yellowish crystals; mp 132—135 °C (lit,[8] 132—135 °C).

Perchlorate (**5b**) was obtained as follows. 3-Methylthiazolidine-2-thione (2.7 g) was dissolved in 2.5 g of dimethyl sulfate. A vigorous exothermic reaction occurred when the mixture was heated up to 60 °C. The reaction temperature was kept below 100 °C. After the exothermic reaction was over, the mixture was stirred at 90 °C for 30 min. The mixture was poured into a saturated aqueous solution of sodium perchlorate giving 5.0 g (85%) of a pale yellowish precipitate, which was washed several times with ether and dried over phosphorous pentoxide *in vacuo*. The precipitate was so hygroscopic that its mp could not be determined. The structure of the salt was confirmed by its NMR spectrum (Table 1).

*2,3,5,6-Tetrahydrothiazolo[2.3-b]thiazolium Salts (**6**).* Carbonium chloride (**6a**) was prepared by the method in literature.[9] Bis(*β*-chloroethyl)amine hydrochloride (7.14 g) was dissolved in a solution of pyridine (10 ml) and water (4 ml). Carbon disulfide (2.4 ml) was added dropwise into the mixture with stirring for one hour; the mixture was kept below 10 °C. The white turbid solution thus formed was stirred at room temperature for 45 min, and warmed at 40 °C for 20 min. The reaction mixture was cooled in an ice box giving 7.9 g (90%) of a colorless precipitate. The precipitate was then dissolved in a minimum amount of water and reprecipitated by addition of ethanol giving colorless crystals; mp 93—95 °C (lit.,[9] 95 °C).

Treatment of **6a** with saturated aqueous solution of sodium perchlorate gave a colorless precipitate; mp 158—159 °C (recrystallized from acetonitrile).

Found: C, 24.40; H, 3.26; N, 5.70%. Calcd for $C_5H_8ClNO_4S_2$: C, 24.57; H, 3.36; N, 5.61%.

*3-Dimethylamino-2,4-benzodithiepan-3-ylium Perchlorate (**7**).* *o*-Xylylene dibromide (5.3 g) was added to a suspension of sodium *N,N*-dimethyldithiocarbamate (3.6 g) in 50 ml of dioxane. The mixture was stirred at 60 °C for 5 hr, then poured onto cold water (*ca.* 150 ml) giving 2.0 g of a white precipitate of *o*-xylylene bis(dithiocarbamate) (**8**); mp 124.5—125.5 °C (recrystallized from benzene); UV (EtOH): $\lambda_{max}$ 250 and 275.5 mμ. The IR spectrum showed several absorption bands due to –S–CS–N<.

Found: C, 48.84; H, 5.86; N, 8.14%. Calcd for $C_{14}H_{20}N_2S_4$: C, 48.79; H, 5.85; N, 8.13%.

The filtrate was extracted with benzene and the aqueous solution was treated with an excess of sodium perchlorate giving 2.5 g (40%) of a white precipitate. Recrystalliza-

tion of the precipitate from ethanol and benzene gave colorless needles (**7**); mp 205—207 °C (dec.).

Found: C, 41.13; H, 4.24; N, 4.46%. Calcd for $C_{11}H_{14}ClNO_4S_2$: C, 40.80; H, 4.36; N, 4.33%.

*Reaction of* ***5a*** *with Sodium Methoxide.* **5a** (2.9 g) and sodium methoxide (1.1 g) were added to 25 ml of dioxane. The mixture was stirred at 100 °C for 3 hr and then poured into water. The mixture was extracted with ether. The ethereal layer was dried over anhydrous sodium sulfate, and the solvent evaporated *in vacuo*. Distillation of the residue gave 0.70 g (70%) of 3-methylthiazolidine-2-one; bp 85—87 °C/0.3 mmHg (lit,[18] 84—85 °C/0.2 mmHg); IR (neat): 1665 $cm^{-1}$ (C=O). The IR spectrum of the product was in agreement with that of an authentic sample.

*Hydrolysis of* ***5a***. **5a** (0.02 mol) was dissolved in 20 ml of water. The mixture was heated at 60 °C for 3 hr and then extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate and the solvent evaporated, giving 1.0 g of a yellowish oily residue. The IR spectrum of the residue was essentially the same as that of 3-methylthiazolidine-2-thione.

*Reaction of* ***5a*** *with Aniline.* **5a** (0.01 mol) and aniline (0.01 mol) were dissolved in 40 ml of acetic acid. The mixture was heated at 100 °C for 1 hr. The solvent was removed under reduced pressure giving a solidified residue. Recrystallization of the residue from acetonitrile gave crystals of the hydroiodide of 2-phenylimino-3-methylthiazolidine in 58% yield; mp 215—220 °C.

Found: N, 8.60%. Calcd for $C_{10}H_{13}IN_2S$: N, 8.75%.

An aqueous solution of the hydroiodide was treated with sodium methoxide giving the precipitate of 2-phenylimino-3-methylthiazolidine; mp 90—92 °C (recrystallized from methanol); IR (KBr): 1610 $cm^{-1}$ (C=N).

Found: C, 61.97; H, 6.49; N, 14.63%. Calcd for $C_{10}H_{12}N_2S$: C, 62.48; H, 6.29; N, 14.58%.

*Reaction of* ***5a*** *with Tosylhyrdazine.* Tosylhydrazine (3.7 g) was suspended in a solution of **5a** (0.02 mol) in 40 ml of ethanol. The suspension was stirred at 55—60 °C for 4 hr. The reaction mixture turned into a clear solution. The resulting mixture was cooled in an ice box giving 2.7 g (62%) of a precipitate of the hydrazone. Recrystallization of the precipitate from ethanol gave colorless needles; mp 215 °C (dec.); IR (KBr): 1590 $cm^{-1}$ (C=N).

Found: C, 46.08; H, 5.29; N, 15.06%. Calcd for $C_{11}H_{15}N_3O_2S_2$: C, 46.31; H, 5.30; N, 14.73%.

*Reaction of* ***5a*** with Triethylamine. **5a** (0.01 mol) was dissolved in a solution of triethylamine (1.0 g) in 20 ml of DMSO. The mixture was heated at 80 °C for 4 hr and then poured onto cold water giving 0.70 g (52%) of the precipitate of 3-methylthiazolidine-2-thione. The IR and UV spectra of the product were in agreement with those of an authentic sample.

*Reaction of* ***5a*** *with Sodium* N,N-*Dimethyldithiocarbamate.* **5a** (0.01 mol) was dissolved in a solution of sodium dimethyldithiocarbamate (3.0 g, 0.015 mol) in 40 ml of DMF. The reaction mixture was heated at 70 °C for 5 hr and then poured onto cold water. The mixture was extracted with benzene. The benzene layer was dried over anhydrous sodium sulfate and the solvent evaporated *in vacuo* giving a half-solid residue (1.3 g). Thin layer chromatography (tlc) was applied to separation and identification of the residue. The chromatogram was developed over silica gel (G. E. Merck Ag., Darmstadt) by dipping the top end of the glass plate in anhydrous ether. The plate was then exposed to iodine vapor showing two spots which were found to be those of methyl *N,N*-dimethyldithiocarbamate ($R_f$=0.98) and 3-methylthiazolidine-2-thione ($R_f$=0.46). The result was confirmed by UV spectroscopy.

*Reaction of* ***6b*** *with Sodium Cyanide.* **6b** (5.4 g, 0.02 mol) and sodium cyanide (1.0 g) were dissolved in 30 ml of DMF. The mixture was heated at 50—60 °C for 6 hr giving the precipitate of sodium perchlorate which was then filtered off. The filtrate was concentrated under reduced pressure and cooled in an ice box giving 3.2 g (93%) of a pale yellowish precipitate. Recrystallization of the solid from ethanol gave colorless crystals (**10**): mp 72—73 °C; IR (KBr): 2260 $cm^{-1}$(C≡N); NMR ($CDCl_3$): $\delta$ 3.37.

Found: C, 42.62; H, 4.61; N, 16.44%. Calcd for $C_6H_8N_2S_2$: C, 41.86; H, 4.68; N, 16.28%.

*Reaction of* ***6b*** *with Sodium* N,N-*Dimethyldithiocarbamate.* **6b** (5.4 g) and sodium *N,N*-dimethyldithiocarbamate (3.6 g) were dissolved in 20 ml of DMF. The mixture was heated at 60 °C for 2 hr, then poured onto cold water giving 4.4 g (83%) of a white precipitate. Recrystallization of the precipitate from ethanol and acetonitrile gave colorless needles (**11**); mp 142—143 °C. The IR spectrum of the product showed several absorption bands due to –S–CS–N<. The UV spectrum was in agreement with that of an equimolar mixture of methyl *N,N*-dimethyldithiocarbamate and 3-methylthiazolidine-2-thione.

Found: C, 36.28; H, 5.22; N, 10.18%. Calcd for $C_8H_{14}N_2S_4$: C, 36.10; H, 5.26; N, 10.52%.

The reaction of **6b** (0.01 mol) with sodium *N,N*-diethyldithiocarbamate (0.01 mol) carried out as in the case of sodium *N,N*-dimethyldithiocarbamate gave *N*-(*β*-*N'*,*N'*-diethyldithiocarbamoyl)ethylthiazolidine-2-thione in 80% yield; mp 74—75 °C (recrystallized from ethanol).

Found: C, 40.74; H, 6.21%. Calcd for $C_{10}H_{18}N_2S_4$: C, 40.81; H, 6.17%.

*Hydrolysis of* ***7***. Perchlorate **7**(0.01 mol) was dissolved in 10 ml of water. The mixture was heated at 60 °C for 3 hr and then extracted with benzene. The benzene layer was dried over anhydrous sodium sulfate and the solvent evaporated *in vacuo* giving a small amount of a yellowish oil; IR (neat): 1650 $cm^{-1}$(C=O). The oil discolored an aqueous solution of iodine and gave the mercury mercaptide on treatment with mercuric chloride indicating the presence of the mercapto group.

*Reaction of* ***7*** *with Sodium* N,N-*Dimethyldithiocarbamate.* **7** (0.3 g) and sodium dimethyldithiocarbamate (0.5 g) were dissolved in 20 ml of DMF. The mixture was stirred at 60 °C for 30 min and then poured onto cold water giving 0.35 g (98%) of a white precipitate. The product was identical with *o*-xylylene bis(dithiocarbamate) (**8**).

*Kinetic Measurements. Hydrolyses (Mode A).* The equipment and procedures were the same as those employed previously.[5] The rates of hydrolyses of the carbonium perchlorates were spectrometrically measured at 30 °C by following the disappearance of the cation. Pseudo-first-order rate constants ($k_{obs}$) were calculated from the plots of 2.303 log $(OD)_0/(OD)_t$ *vs.* time. The plots of $k_{obs}$ against [$OH^-$] for the cations were linear in the pH range 7.5—9.0. The second-order rate constant ($k_a$) for reaction with hydroxide ion was calculated from the slopes of plots of $k_{obs}$ *vs.* [$OH^-$] (Fig. 2).

*Reactions with Sodium* N,N-*Dimethyldithiocarbamate (Mode B).* The procedures were the same as those employed previously.[3,5] The rates of reactions with the dithiocarbamate anion were measured at 30 °C by following the disappearance of the anion. All reactions were carried out in DMF under equimolar conditions. At various time intervals the dithiocarbamate ion was gravimetrically determined from the quantity of the nickel chelate precipitated by treatment of the aqueous solution of the sample with an excess of a sa-

turated aqueous solution of nickel chloride. The second-order rate constants ($k_b$) were calculated from the slopes of plots of $1/a-x$ *vs.* time (Fig. 3).

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