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Tri(hetero)substituted Carbonium Ions. III. Ring-size Effects on the Dual Reactivities of 2-Dimethylamino-1,3-dithiolanylium Ion and Its Ring Analogs as Ambident Electrophiles[*1]

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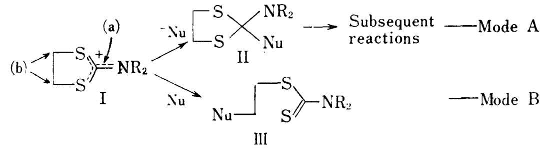
The following ring analogs of 2-dimethylamino-1,3-dithiolanylium perchlorate (Ia) were prepared: 2-dimethylamino-1,3-dithianylium perchlorate (IV), 2-dimethylamino-1,3-dithiepanylium perchlorate (V) and an open-chain analog, bis(methylthio)dimethylaminocarbonium perchlorate (VI). In order to investigate the structural effect on the reactivities of the tri(hetero)-carbonium ions at two reactive sites, *i. e.*, the centered carbon (sp^2) (a) and the *S*-methylene carbon (sp^3) atoms (b), the reactions of these carbonium ions with hydroxide ion (mode A) and with *N*,*N*-dimethyldithiocarbamate ion (mode B), respectively, were studied at 30°C. The rates of mode A of these carbonium ions, relative to that of Ia, are 1 : 15.0 (IV) : 32.5 (V) : 1.06×10^4 (VI), and of mode B are 1 : 6.5 : 23.5 : $\approx2.0\times10^4$. In their electronic spectra a definite trend that as the ring-size increases there is a strong shift of absorption maxima toward the lower energies was observed. The fact suggests that the stability of the carbonium ion decreases with an increase in ring-size. On the basis of the schematic energy profiles for the two modes as well as the structural and kinetical aspects, it has been assumed that one of common factors contributing to the ring-size effect on both reactivities would be the stability of the carbonium ion.

In the preceding paper[1)] we have reported that 2-dialkylamino-1,3-dithiolanylium ion (I) is an ambident electrophile with two reactive sites, (a) and (b), and reacts with the nucleophile ($^-$Nu) *via* reaction mode A and B to give cyclic product II (or its pyrolytic product) and ring-opening product III, respectively, according to the nucleophilicity of the attacking reagent used.



Furthermore, it has been assumed[1)] that the reaction course is decided by the relative stability of the cation I to the kinetical adduct II. Thus, it is anticipated that both reaction course and dual reactivities of this type of tri(hetero)substituted carbonium ions would depend largely upon the structure of the carbonium ions.

In the present paper we will describe the ring-size effect on the dual reactivities of 2-dimethylamino-1,3-dithiolanylium ion (Ia) and its ring analogs as ambident electrophiles and discuss structural factors controlling the reactivities of these carbonium ions.

Results

Preparations of Carbonium Salts. Tri(hetero)substituted carbonium ions studied here are 2-dimethylamino-1,3-dithiolanylium ion (Ia) (five-membered), 2-dimethylamino-1,3-dithianylium ion (IV) (a six-membered analog), 2-dimethyl-amino-1,3-dithiepanylium ion (V) (a seven-membered analog) and bis(methylthio)-dimethylamino-

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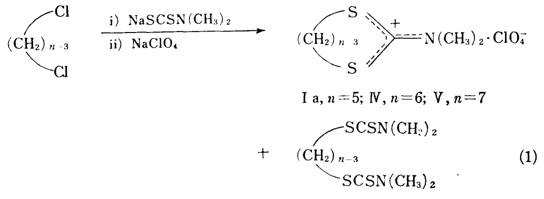
[*1] Presented at the 18th Symposium on Organic Reaction Mechanisms, Kyoto, October, 1967.

1) Part II: T. Nakai and M. Okawara, *Tetrahedron Lett.*, **1967**, 3835; This Bulletin, **43**, 1864 (1970).

carbonium ion (VI) (an open-chain analog).[2] All these carbonium ions were isolated as perchlorates.

Cyclic carbonium perchlorates, Ia, IV and V, were prepared by the equimolar reaction of the corresponding α,ω-dichloroalkane with sodium *N*,*N*-dimethyldithiocarbamate in ethanol followed by treatment with sodium perchlorate (Eq. (1)).[3] In all cases the reaction was accompanied by the formation of the corresponding bis(dithiocarbamate) (VII), arising mainly from the interaction between the cyclic carbonium ion formed and the dithiocarbamate anion *via* mode B.[4] The yield of disubstituted product VII under the equimolar condition increases with the ring-size *n* (Table 1). The fact suggests that with an increase in ring-size participation of the dithiocarbamate function might be favorably involved in the second substitution process from the monosubstituted intermediate to the disubstituted VII.[4,5]

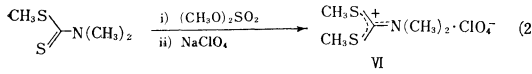
Open-chain carbonium perchlorate (VI) was prepared by methylation of *S*-methyl *N*,*N*-dimethyldithiocarbamate with dimethyl sulfate[6] followed by treatment with sodium perchlorate (Eq. (2)).



I a, *n*=5; IV, *n*=6; V, *n*=7

VII

(1)



VI

(2)

These carbonium ions were identified by elemental analyses and NMR spectra. Characterization and spectral data of carbonium perchlorates obtained are summarized in Table 1, along with yields of disubstituted product VII.

Reactions as Ambident Electrophiles. It has been reported that the reaction of five-membered cation Ia with hydroxide ion yielded β-mercaptoethyl *N*,*N*-dimethylthiolcarbamate (VIII, $n=5$).[1] Similarly six-membered IV and open-chain VI gave γ-mercaptopropyl thiolcarbamate (VIII, $n=6$)[3] and methyl thiolcarbamate, respectively. These hydrolytic products are best explained as the result of initial attack of hydroxide ion at the reactive site (a) followed by proton transfer (Eq. (3)). On the other hand, it has been shown that the reaction of Ia with *N*,*N*-dimethyldithiocarbamate anion yielded ethylene bis(dithiocarbamate) (VII, $n=5$) in the quantitative yield.[1] Similarly reactions of other cyclic carbonium ions and open-chain VI with the dithiocarbamate anion afforded the corresponding bis(dithiocarbamate) (VII) and methyl *N*,*N*-dimethyldithiocarbamate, respectively. The formation of these products may be explained by attack of the dithiocarbamate anion at site (b) presumably through the S$_N$2-like mechanism (Eq. (4)).[1,4]

Thus, in order to estimate both reactivities at the two sites of each carbonium ion, the rates of reactions of the carbonium ion with hydroxide and the dithiocarbamate ions selected as typical reactions of mode A and B, respectively, were measured.

The reactions of the carbonium salt with hydrox-

TABLE 1. CARBONIUM PERCHLORATES

Cation	Ring-size *n*	Yield %	Mp °C	UV (H_2O)[a] λ_{max} (mμ)	NMR,[b] δppm			VII[c] Yield, %
					-S-CH_2-	N-CH_3	-CH_2-C$\underline{H}_2$-CH_2	
Ia	5	61	179—181	249	4.06(s)	3.58(s)		8
IV	6	27	97—99	262	4.43(t)[d]	3.55(s)	2.27(t)[d]	23
V	7	*ca.* 10	58—60	275	3.47(m)[e]	3.61(s)	2.10(m)[e]	48
VI	∞	76	84—86	276	2.85(s)[f]	3.70(s)		—

a) Accurate molar extinction coefficients (ε) could not be obtained due to occurrence of partial hydrolyses during measurements; however, the observed values were 0.70—1.42 × 10^4.

b) Multiplicity: s=singlet, t=triplet, m=multiplet.

c) The disubstituted product isolated as a by-product (see the text).

d) J=7.0 Hz. e) The center of the multiplet. f) The *S*-methyl protons.

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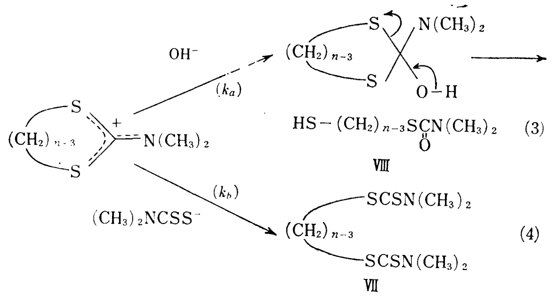
[2] The cation may be also termed *N*,*N*-dimethyl-*S*,*S*′-dimethyldithiocarbamidium ion: J. L. Richards, D. S. Tarball and E. H. Hoffmeister, *Tetrahedron*, **24**, 6485 (1968). For the nomenclature on other cations, see Ref. 3 in the preceding paper.[1]

[3] K. C. Kennard and J. A. VanAllan [*J. Org. Chem.*, **24**, 470 (1959)] have prepared *p*-toluene sulfonates of the five- and six-membered carbonium ions by the reactions of ω-hydroxyalkyl *N*,*N*-dimethyldithiocarbamates with *p*-toluenesulfonyl chloride in benzene or DMF.

[4] T. Nakai, Y. Ueno and M. Okawara, *Tetrahedron Lett.*, **1967**, 3831; This Bulletin, **43**, 156 (1970).

[5] T. Nakai, H. Kawaoka and M. Okawara, This Bulletin, **42**, 508 (1969).

[6] H. V. Rinteln and O. Riester [*Mitt. Forshungslab. Agfa Leverkusen-München*, **1**, 65 (1955); *Chem. Abstr.*, **51**, 7013 (1957)] have reported the formation of the methyl sulfate salts of bis(alkylthio)dialkylaminocarbonium ions, but no carbonium salts were isolated.



ide ion and water in aqueous solutions were undertaken in buffer solutions at 30°C under pseudo-first-order conditions. The rate of disappearence of the carbonium ion was followed by spectrophotometry. As the hydroxide concentration is essentially constant, the rate equation may be represented as

$$k_{\text{obs}} = k_{H_2O} + k_a[OH^-]$$

where $[OH^-]$ and k_{obs} refer to the hydroxide concentration and the observed pseudo-first-order rate constant, respectively. The plots of k_{obs} against $[OH^-]$ for these carbonium ions were linear in the ranges of the hydroxide concentrations studied. From the slopes and intercepts of these plots, we obtained the values of the second-order rate constant (k_a) for reaction with hydroxide ion and the pseudo-first-order rate constant (k_{H_2O}) for reaction with water (Table 2).

TABLE 2. HYDROLYSES OF CARBONIUM PERCHLORATES

Cation	Ring-size n	$[OH^-]$, mol/l	$10^5 k_{\text{obs}}$ sec^{-1}	$10^6 k_{H_2O}$ sec^{-1}	k_a mol^{-1}l sec^{-1}
Ia	5	6.31×10^{-6}	0.397		
		12.3	0.650	3.5	0.51
		16.6	0.825		
IV	6	0.603×10^{-6}	0.617		
		2.00	1.39	1.0	7.60
		3.02	2.25		
		5.25	3.33		
V	7	0.407×10^{-6}	0.650		
		2.00	3.30	0.5	16.6
		3.02	5.05		
VI	∞	5.13×10^{-9}	8.4		
		6.46	9.0		
		7.94	10.4	56	5.4×10^3
		12.6	12.3		

On the other hand, the reaction of the carbonium ion with sodium *N,N*-dimethyldithiocarbamate was studied in dimethylformamide (DMF) at 30°C under the equimolar condition. The rate of reaction was measured by following the disappearance of the dithiocarbamate anion using the previously-reported method.[4] From the slopes of the second-order rate plots (Fig. 1), we obtained the values of the rate constant (k_b) for reaction of the cyclic cations with the dithiocarbamate ion. The rate of reaction of open-chain VI with the anion was too large to be accurately measured by this method. The value of k_b for VI was found to be approximately 26.0 mol^{-1}l sec^{-1}. The values of the relative k_b obtained are shown in Table 3 together with those of the relative k_a.

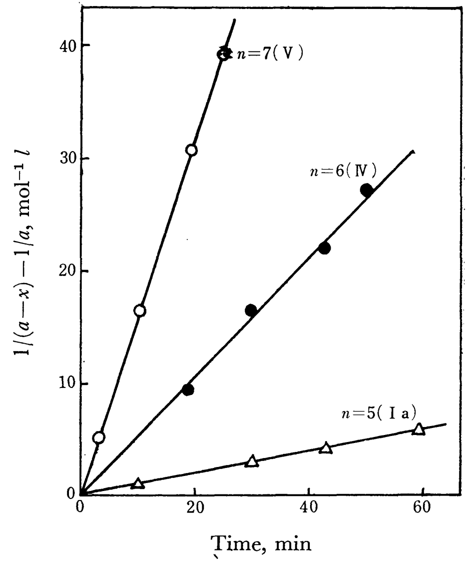


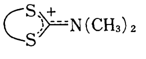
Fig. 1. Second-order rate plots for the cyclic carbonium ions at 30°C under the equimolar condition; a=0.03 mol/l.

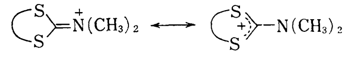
TABLE 3. THE RELATIVE k_a AND k_b FOR THE CARBONIUM IONS AT 30°C

Cation	Ring-size n	Mode A Rel. k_a	Mode B Rel. k_b
Ia	5	1.0	1.0
IV	6	15.0	6.5
V	7	32.5	23.8
VI	∞	1.06×10^4	$\approx 2.0\times10^4$

Discussion

Structural Aspects. The carbonium ions concerned are strongly stabilized by accepting electrons from α-hetro atoms, and so the positive charge is widely delocalized as expressed in formula IX.


IX


X XI

The *exo*-iminium structure X would be more important rather than the sulfonium XI if the cation is not subject to any steric requirements as in the case of open-chain VI, since the electron-donating power of the dimethylaminogroup is much larger than the alkylthio groups. In the electronic spectra of these carbonium salts (Table 1), there is a definite trend that as the ring-size increases there is a strong shift of absorption maxima (λ_{max}) toward the lower energies (the longer wavelengths) (Fig. 2).

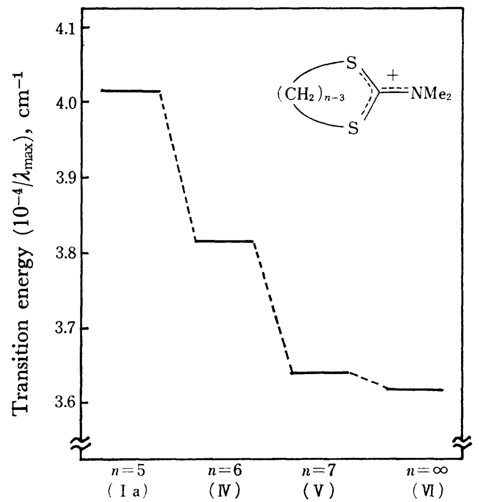


Fig. 2. The ring-size effect on the transition energy of the carbonium ions.

A similar trend has also been observed in the electronic spectra of a series of cyclic alkenylcarbonium ions.[7] This observation has been interpreted by the idea that one of factors contributing to the ring-size effect on a band shift may be that 1,3-π-overlap will be progressively more significant as the bond angle between the three conjugating carbon atoms decreases. The ring-size effect on band shifts is implicit in Mulliken's[8] and Walsh's[9] treatment of bonding in triatomic systems.

Appling the idea to the tri(hetero)carbonium ions concerned, the spectral trend suggests that α-hetero atoms stabilize the ground state more than the excited state[10] and, hence, as the ring-size decreases, the ground state is more stabilized presumably due to the more developed 1,3-overlap in the ring system, *i. e.*, $\overset{+}{\overbrace{S{\cdots}C{\cdots}S}}$, as found experimentally. In other words, contribution of the sulfonium structure XI to stabilization of the carbonium ion progressively increases with decrease in ring-size.

The ring-size effect on stabilization described above is also implicit in the NMR spectra (Table 1). A change in ring-size appears to affect the chemical shifts of the *S*-methylene protons in the ring more greatly rather than those of the *N*-methyl protons. The *S*-methylene protons of five-membered Ia are deshielded more than those of other ring analogs presumably due to more favorable contribution of the sulfonium structure.

Ring-size Effects on Reactivities. The kinetical results obtained indicate that reactivities of these carbonium ions at the two reactive sites are progressively enhanced as the ring-size increases (Fig. 3). In the light of these results our task is now to consider factors contributing to the ring-size effects on reactivities.

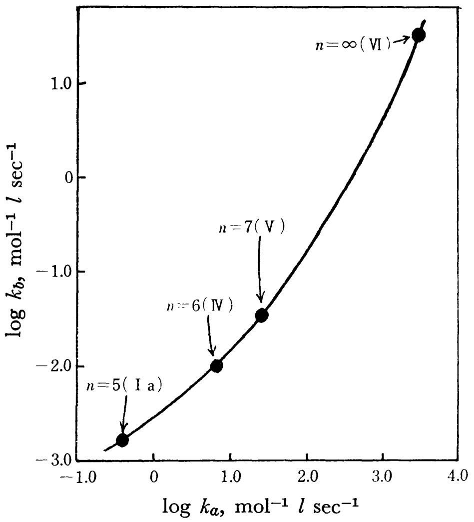


Fig. 3. Plot of log k_a (mode A) *vs.* log k_b (mode B).

As has been assumed,[1] the mode A process initially yields a kinetically-controlled product and the activation free energy ($\Delta F_A^{\ddagger}$) is small since the primary process of mode A involves an association between a cation and an anion. Thus, the reaction of the carbonium ion with hydroxide ion might be a expressed as follows:

$$R^+ + OH^- \overset{K}{\rightleftharpoons} ROH \underset{\text{(fast)}}{\longrightarrow} VIII$$

where R^+ and ROH are the carbonium ion concerned and the carbinol, respectively. The overall rate constants (k_a) would be proportional to the equilibrium constant (K). Consequently the rate of mode A should depend upon the relative position between R^+ and ROH in the energy diagram.

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[7] G. A. Olah, C. U. Pittman, Jr., and M. C. R. Symons, "Carbonium Ions," Vol. 1, G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, New York (1968), Chapter 5.

[8] R. S. Mulliken, *Can. J. Chem.*, **36**, 10 (1958).

[9] A. D. Walsh, *J. Chem. Soc.*, **1953**, 2266.

[10] Another definite evidence for this idea has been presented that as the methylthio group in tris(methylthio)carbonium ion is progressively replaced by the dimethylamino group, there is a strong shift of absorption maxima to the higher energies (the shorter wavelengths): T. Nakai, K. Hiratani and M. Okawara, the 3rd Symposium on Organic Sulfur Chemistry, Tokyo, 1969. Furthermore, this idea has been confirmed by simple HMO calculations: T. Nakai and M. Okawara, the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, 1970.

Although it is easy to estimate the stability of ROH, the relative stability of R^+ may be evaluated in terms of the absorption maximum ($\lambda_{\max}$) as described above.

The kinetical result shows that increasing k_a-values are paralleled by increasing ring-sizes, *i. e.*, by decreasing stabilities of the carbonium ions; this fact suggests that an increase in ring-size would lower the stability of the carbonium ion, at least to a more extent, rather than that of the carbinol. On the basis of the schematic energy profile for mode A (Fig. 4),[11] the free energy gap between the cation and the carbinol (ΔF_A) increases as the ring-size increases. In short, it may be noted that the rate of mode A depends upon the stability of the carbonium ion varying mainly with ring-size.

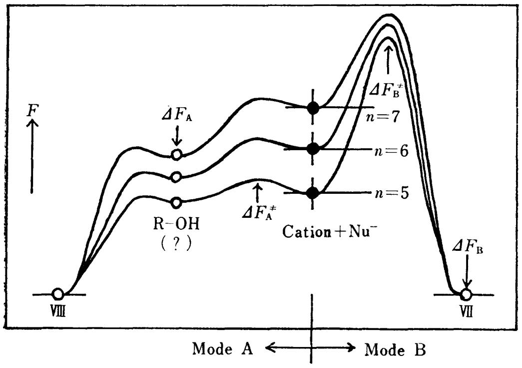

Fig. 4. Schematic energy profiles for mode A and B. Strictly speaking, the energy content of the initial system, cation and Nu^-, depends on the nature of Nu^-. However, since the nucleophile remains constant, this energy content of the respective mode is determined solely by the nature of the cation.

On the other hand, the reaction of mode B is irreversible. Accordingly it can be assumed[1,11] that in contrast to mode A the rate of reaction with the dithiocarbamate ion is determined by the magnitude of the activation free energy ($\Delta F_B^{\neq}$) rather than that of ΔF_B in the schematic energy profile for mode B (Fig. 4). The kinetical result shows that the rate of mode B increases in the same order as that of mode A (Fig. 3); this fact suggests that an increase in ring-size would lower the stability of the carbonium ion, at least to a more extent, rather than that of the transition state. In consequence an increase in ring-size results in a stepwise lowering of the energy gap ($\Delta F_B^{\neq}$), as found experimentally. However, large differences in rate (k_a and k_b) between seven-membered V and open-chain VI, of which stabilities appear to be almost the same from their absorption maxima, cannot reasonably explained in the present stage.

In any case, these considerations permit only a qualitative conclusion that one of significant factors controlling both reactivities may be the stability of the ground state of the carbonium ion varying with the extent of 1,3-overlap in the ring system.

Experimental

General. Melting and boiling points are uncorrected. The IR and UV spectra were recorded with Hitachi EPI-S2 and EPS-2 spectrometers, respectively. The NMR spectra were determined with a Varian Associates A-60 spectrometer. Chemical shifts are reported in parts per million (ppm) from tetramethylsilane as an internal standard.

2-Dimethylamino-1,3-dithiolanylium Perchlorate (Ia). The carbonium perchlorate was prepared by the procedure reported in the previous paper[1]: mp 179—180°C.

2-Dimethylamino-1,3-dithianylium Perchlorate (IV). 1,3-Dichloropropane (12.3 g, 0.11 mol) was added to a solution of 20.0 g (0.11 mol) of sodium *N*,*N*-dimethyldithiocarbamate in 75 m*l* of ethanol. The mixture was stirred at 60°C for 6 hr. The mixture was concentrated in reduced pressure and then poured into 100 m*l* of cold water giving 2.4 g (23%) of disubstituted product VII ($n=6$): mp 108—109°C (ethanol).

Found: C, 38.25; H, 6.61; N, 9.87%. Calcd for $C_9H_{18}N_2S_4$: C, 38.26; H, 6.42; N, 9.92%.

The filtrate was extracted with ether and an excess of a saturated aqueous solution of sodium perchlorate was added to the aqueous layer giving 8.0 g (27%) of white precipitates of IV: mp 97—99°C (methanol).

Found: C, 27.73; H, 4.68; N, 5.59%. Calcd for $C_6H_{12}ClNO_4S_2$: C, 27.53; H, 4.62; N, 5.32%.

2-Dimethylamino-1,3-dithiepanylium Perchlorate (V). 1,4-Dichlorobutane (26.5 g, 0.21 mol) was added to a solution of 36.0 g (0.20 mol) of sodium *N*,*N*-dimethyldithiocarbamate in 75 m*l* of ethanol. The mixture was stirred at 60°C for 6 hr. The mixture was concentrated in reduced pressure and poured into cold water giving 12.4 g (48%) of disubstituted product VII ($n=7$): mp 112—113°C.

Found: C, 40.09; H, 6.95; N, 9.71%. Calcd for $C_{10}H_{20}N_2S_4$: C, 40.54; H, 6.80; N, 9.46%.

To the filtrate there was added 100 m*l* of a saturated aqueous solution of sodium perchlorate. The mixture was cooled in an ice box for a few days giving about 4.0 g (10%) of very hygroscopic white precipitates of V. These precipitates were washed several times with ether and dried *in vacuo*: mp 58—60°C.

Found: C, 29.94; H, 4.72; N, 4.97%. Calcd for $C_7H_{14}ClNO_4S_2$: C, 30.49; H, 5.12; N, 4.97%.

Bis(methylthio)-dimethylaminocarbonium Perchlorate (VI). *S*-Methyl *N*,*N*-dimethyldithiocarbamate (13.5 g, 0.01 mol) was dissolved in 12.6 g (0.01 mol) of dimethyl sulfate. When the mixture was heated to 60°C a vigorous exothermic reaction occurred. The reaction temperature was kept below 100°C. After the exothermic reaction ceased the mixture was further stirred at 90°C for 1 hr. The mixture was poured into 100 m*l* of a

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[11] For similar considerations, *e. g.*, see S. Hünig, *Angew. Chem. Internat. Ed.*, 3, 548 (1964) and Ref. 14 in the preceding paper.[1]

saturated aqueous solution of sodium perchlorate giving 19.0 g (76%) of pale yellowish precipitates. The precipitates were washed with ether and recrystallized from methanol giving white precipitates: mp 84—86°C.

Found: C, 23.73; H, 4.68; N, 5.13%. Calcd for $C_5H_{12}ClNO_4S_2$: C, 24.05; H, 4.85; N, 5.61%.

Products. A. Hydrolyses of Carbonium Perchlorates. 2-Dimethylamino-1,3-dithiolanylium perchlorate (Ia) was hydrolyzed to afford β-mercaptoethyl *N,N*-dimethylthiolcarbamate.[1] Similarly 2-dimethylamino-1,3-dithianylium perchlorate (IV) gave γ-mercaptopropyl *N,N*-dimethylthiolcarbamate.[3] No attempt was made to isolate the hydrolytic product of V.

Bis(methylthio)-dimethylaminocarbonium perchlorate (VI) (12.5 g, 0.05 mol) was added to a solution of water (1.0 g, 0.05 mol) and triethylamine (5.0 g, 0.05 mol) in 50 m*l* of dioxane. The mixture was stirred at 80°C for 6 hr, then poured into water. The ethereal extract was dried over sodium sulfate and the solvent evaporated *in vacuo*. Distillation of the residue gave 3.7 g (62%) of *S*-methyl *N,N*-dimethylthiolcarbamate: bp 91—92°C/31 mmHg; $n_D(21°C)$ 1.4964 (lit.[12] bp 115—116°C/89 mmHg; $n_D(30°C)$ 1.4932); IR (neat): 1650 cm^{-1} (C=O). The IR spectrum of the distillate was in agreement with that of the authentic sample.

B. Reactions of Carbonium Perchlorates with Sodium *N,N*-Dimethyldithiocarbamate. The reaction of Ia with sodium *N,N*-dimethyldithiocarbamate afforded ethylene bis(*N,N*-dimethyldithiocarbamate) (VII(n=5)) in the quantitative yield.[1]

Six-membered IV (0.50 g, 2 mmol) and sodium *N,N*-dimethyldithiocarbamate (0.37 g, 2 mmol) were dissolved in 5 m*l* of DMF. The mixture was stirred at 60°C for 4 hr, then poured into water giving 0.48 g (78%) of white precipitates of disubstituted product VII (n=6). The IR spectrum of the product was in agreement with that of the authentic sample. Similarly seven-membered V gave disubstituted product VII (n=7) in the quantitative yield.

Bis(methylthio)-dimethylaminocarbonium perchlorate (VI) (2.5 g, 0.01 mol) and sodium *N,N*-dimethyldithiocarbamate (1.8 g, 0.01 mol) were dissolved in 20 m*l* of DMF. The mixture was stirred at 70°C for 3 hr, then poured into cold water giving 1.1 g (41%) of white precipitates of *S*-methyl *N,N*-dimethyldithiocarbamate: mp 44—46°C (lit.[13] 47°C). The IR spectrum of the product was in agreement with that of the authentic sample. The low yield would be due to partial dissolution of the product in the solvents.

Kinetic Runs. A. Rates of Hydrolyses of Carbonium Salts (Mode A). A Hitachi EPS-2 spectrophotometer equipped with a thermostated cell holder was used to record spectral data. The thermostated cell holder consisted of a brass block through which thermostated water was circulated. A spectrometer cell of 1.0 cm fits into a bore of the block. The rates of all reactions of these carbonium salts with water and hydroxide ion were studied in aqueous solutions buffered with the Clark-Lubs systems. A solution of the desired pH, which initially contained *ca.* 10^{-4} mol/*l* carbonium salt, was prepared in the cell and placed in the holder thermostated at 30±0.3°C. At various time intervals decreases in absorbance at the respective maximum absorption band (λ_{max}) were followed. The semilogarithmic plots of A_0/A_t against time were linear and yielded the observed first-order rate constants (k_{obs}). A typical example of the first-order rate plot is shown in Fig. 5. The second-order rate constants (k_a) for reactions with hydroxide ion, and the pseudo-first-order rate constants (k_{H_2O}) for reactions with water were determined from the slopes and intercepts, respectively, of plots of k_{obs} *vs.* concentrations of hydroxide ion. The values of pH studied ranged from 7.5 to 9.5 and from 5.7 to 6.1 for the cyclic and open-chain carbonium perchlorates, respectively. Results of these experiments are summarized in Table 2.

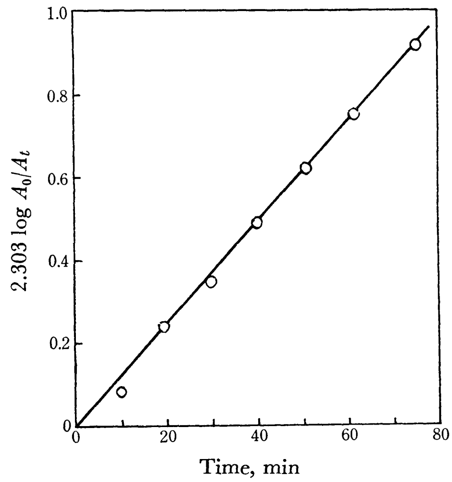

Fig. 5. An example of kinetic runs of carbonium ion IV at 262 mμ; pH=8.48.

TABLE 4. REACTIONS OF IV WITH SODIUM *N,N*-DIMETHYLDITHIOCARBAMATE

Time, min	N-salt formed, g	1/a–x, mol^{-1}l
0	0.122	30.6
15	0.105	35.5
30	0.081	45.9
40	0.074	50.5
50	0.065	57.5

B. Rates of Reactions of Carbonium Salts with Sodium *N,N*-Dimethyldithiocarbamate (Mode B). The rates of reactions with sodium *N,N*-dimethyldithiocarbamate were measured according to the procedures reported in our previous paper.[4] At various time intervals the remaining dithiocarbamate ion was gravimetrically determined from quantities of the nickel chelate precipitated by treatment of the aqueous solution of the sample with an excess of a saturated aqueous solution of nickel chloride. All reactions were carried out at 30°C in DMF solutions under the equimolar condition. The initial concentration was 0.03 mol/*l* for all reactions.

The carbonium perchlorate (0.15 mol) was dissolved in a solution of 0.805 g (0.15 mol) of sodium *N,N*-dimethyldithiocarbamate in 150 m*l* of DMF. The re-

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12) H. Tilles, *J. Amer. Chem. Soc.*, **81**, 714 (1959).

13) J. v. Braun, *Ber.*, **35**, 3368 (1902).

action vessel was placed in a constant-temperature bath at 30±0.2°C. At various time intervals a 25.0-ml aliquot was removed and poured into cold water (*ca.* 100 ml) giving white precipitates of disubstituted product VII. The precipitates were filtered off and the aqueous filtrate was treated with an excess of a saturated aqueous solution of nickel chloride giving green precipitates of the nickel chelate. The nickel chelate was collected in a glass filter. The glass filter was completely dried *in vacuo*. An example of results is given in Table 4.

All plots of $1/a-x$ against time were linear and yielded the second-order rate constants (k_b) for reactions with the dithiocarbamate ion. The reaction of open-chain VI with the anion under these conditions was so fast that accurate measurements could not be made. A very rough estimate for the second-order rate constant for the open-chain analog was 26.0 $\text{mol}^{-1} l \text{ sec}^{-1}$. Results of these experiments are shown in Fig. 1 and Table 3.