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Tri(hetero)substituted Carbonium Ions. I. Neighboring-Group Participation of the *N*,*N*-Dimethyldithiocarbamate Function Involving the Intermediacy of 2-Dimethylamino-1,3-dithiolanylium Ion[*1]

Takeshi NAKAI, Yoshio UENO and Makoto OKAWARA

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

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The equimolar reaction of 1,2-dichloroethane with sodium *N*,*N*-dimethyldithiocarbamate was studied in various solvents. As major products, ethylene bis(*N*,*N*-dimethyldithiocarbamate) and 2-dimethylamino-1,3-dithiolanylium salt (the perchlorate or the tetraphenylborate) were obtained in yields, largely varying with the solvent used. On the basis of the solvent effect on the product ratio, and kinetic experiments it has been verified that neighboring-group participation of the *N*,*N*-dimethyldithiocarbamate function would be involved through the intermediacy of the isolated anchimeric carbonium ion, and that such participation is more predominant in nonpolar aprotic solvents such as dioxane and tetrahydrofuran. The mechanism of the reaction between 2-dimethylamino-1,3-dithiolanylium ion and the dithiocarbamate anion was established.

In previous papers[1-4] we reported that polymers containing the dithiocarbamate function (–$SCSNR_2$) are effective as a photosensitive resin. They were conveniently prepared by polymer reactions since no monomer with the function was readily available. We undertook to prepare *S*-vinyl *N*,*N*-dialkyldithiocarbamate by dehydrochlorination of *β*-chloroethyl dithiocarbamate. However, *β*-chloroethyl dithiocarbamate could not be isolated from the equimolar reaction of 1,2-dichloroethane with *N*,*N*-dialkyldithiocarbamate anion, but some unexpected observations described below were made. It was found that the vacuum pyrolysis of ethylene bis(*N*,*N*-dialkyldithiocarbamates) afforded *S*-vinyl *N*,*N*-dialkyldithiocarbamates in good yields, and their radical polymerizabilities were compared with those of the oxygen analogs.[5]

The observations obtained in the equimolar reaction between 1,2-dichloroethane (I) and sodium *N*,*N*-dimethyldithiocarbamate hydrate (II) are as follows: (i) the expected monosubstituted product, *β*-chloroethyl *N*,*N*-dimethyldithiocarbamate (III) could not be obtained at all; (ii) as major products, the disubstituted ethylene bis(*N*,*N*-dimethyldithiocarbamate) (IV) and 2-dimethylamino-1,3-dithiolanylium ion[*2] (V) (as the perchlorate) were isolated in yields varying with the solvent. The results led us to study the mechanism of this equimolar reaction.

In the present paper we describe neighboring-group participation of the *N*,*N*-disubstituted dithiocarbamate function involving the intermediacy of the isolatable anchimeric cation[*3] (V) in the reaction of 1,2-dichloroethane with the dithiocarbamate anion, mainly on the basis of the solvent effect on the product ratio and kinetic experiments.

Results and Discussion

The Solvent Effect on the Product Ratio. The equimolar reactions of 1,2-dichloroethane (I) with sodium *N*,*N*-dimethyldithiocarbamate (II) were undertaken at 60°C for 6 hr in various solvents. The dithiocarbamate anion completely disappeared during reaction under this condition. Ethylene bis(*N*,*N*-dimethyldithiocarbamate) (IV) and 2-

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[*1] Part of this work has been published. T. Nakai, Y. Ueno and M. Okawara, *Tetrahedron Lett.*, **1967**, 3831.

1) M. Okawara, H. Yamashina, K. Ishiyama and E. Imoto, *Kogyo Kagaku Zasshi*, **66**, 1383 (1963).

2) M. Okawara, K. Morishita and E. Imoto, *ibid.*, **69**, 761 (1966).

3) M. Okawara, M. Ori, T. Nakai and E. Imoto, *ibid.*, **69**, 766 (1966).

4) M. Okawara and T. Nakai, *Bull. Tokyo Inst. Technol.*, **78**, 1 (1967).

5) T. Nakai, K. Shioya and M. Okawara, *Makromol. Chem.*, **108**, 95 (1967).

[*2] Carbonium ion is more precisely expressed as 2-dimethylamino-1,3-dithiolan-2-ylium ion. In our papers "1,3-dithiolanylium ion" means "1,3-dithiolan-2-ylium ion."

[*3] The term "anchimeric cation" refers to cyclic carbonium ion formed *via* intramolecular S_N reaction involving a neighboring group, such as V and VII.

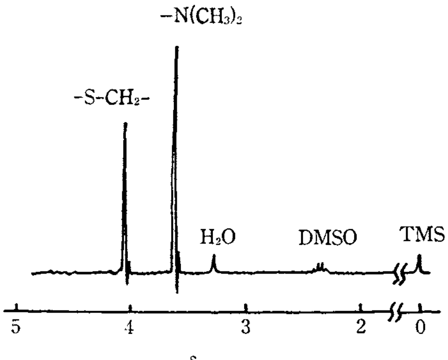
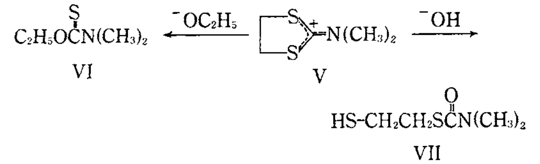


Fig. 1. The NMR spectrum of 2-dimethylamino-1,3-dithiolanylium perchlorate (Vb) in DMSO-d_6.

dimethylamino-1,3-dithiolanylium salt (V) were obtained as major products. Ethylene bis(dithiocarbamate) was identified by comparisons of both spectral data with that of authentic sample and the mixed mp determination.

The dithiolanylium salt (V) was isolated as perchlorate by treatment of an aqueous layer of the reaction mixture with sodium perchlorate. The structure of the perchlorate Vb was confirmed by elemental analysis and an independent preparation according to the reported method.[6] The NMR spectrum (Fig. 1) of the perchlorate was superimposable, exhibiting two singlet signals at δ 4.08 ($-CH_2-S-$) and 3.62 ppm (CH_3-N). Dithiolanylium ion was also isolated as the tetraphenylborate (Vc) in higher yields than the perchlorate Vb, but not quantitatively because Vc dissolved in water. The formation of dithiolanylium ion can be explained by the intramolecular nucleophilic substitution (S_Ni) reaction of β-chloroethyl dithiocarabamate (III) formed.

The reaction of I with II in ethanol afforded ethyl thioncarbamate (VI) and β-mercaptoethyl thiolcarbamate (VII) as well as major products described above. The thioncarbamate (VI) was identified by comparison of physical properties and spectral data of the authentic sample. The thiolcarbamate (VII) exhibits a strong absorption band at 1650 cm^{-1} due to $\nu_{C=O}$ for $-S-CO-N<$ and was treated with lead acetate to give a precipitate of the lead mercaptide. The formation of VI was not observed with reactions in other solvents than ethanol. Separate experiments suggested that these by-products were formed through ethanolysis and hydrolysis of 2-dimethylamino-1,3-dithiolanylium ion (V), respectively.[7]



The product compositions for the equimolar reactions in various solvents are given in Table 1. The results indicate that the product ratio is largely dependent on the nature of the solvent. From the effect on the product ratio, solvents may be classified into three groups; dipolar protic (EtOH, EGOH), dipolar aprotic (DMF, DMSO, CH_3CN) and nonpolar aprotic (dioxane, THF). The yield of IV increases in the order: nonpolar>dipolar aprotic>dipolar protic. It may be noted that, especially in dioxane and THF, the disubstituted product (IV) was more favorably formed under the equimolar condition. The fact cannot be

TABLE 1. PRODUCTS FROM THE EQUIMOLAR REACTIONS OF I WITH II
Reaction temp.: 60°C; time, 6 hr

Solvent	Composition (% based on II)		Others
	Ethylene bis-dithiocarbamate (IV)	2-Dimethylamino-1,3-dithiolanylium salt (Vc)[a]	
Ethanol (EtOH)	8.4	61.4	5.5,[b] 3.9[c]
Ethylene glycol (EGOH)	trace	59.6	trace[c]
Dimethylformamide (DMF)	23.0±0.5[d]	57.3±2.0	trace
Dimethylsulfoxide (DMSO)	13.4	51.5	trace
Acetonitrile (CH_3CN)	11.2	67.0	trace
Dioxane	56.9±0.1	29.0±1.0	trace
Tetrahydrofuran (THF)	67.5±2.0	21.4±2.0	trace

a) 2-Dimethylamino-1,3-dithiolanylium chloride (Va) formed could not be quantitatively isolated as the tetraphenylborate Vc (see the text).
b) *O*-Ethyl *N*,*N*-dimethylthioncarbamate (VI).
c) β-Mercaptoethyl *N*,*N*-dimethylthiolcarbamate (VIII).
d) Average and deviation of values obtained by two experiments.

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[6] C. Kennard and J. A. VanAllan, *J. Org. Chem.*, **24**, 470 (1959).

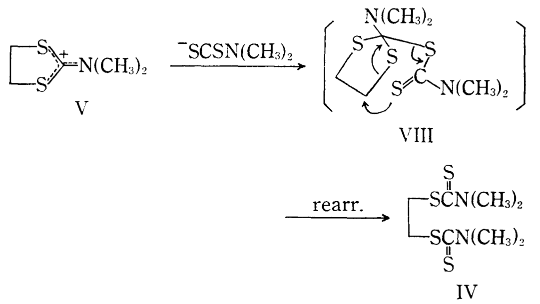
[7] T. Nakai and M. Okawara, *Tetrahedron Lett.*, **1967**, 3835.

explained by two successive simple S_N2 reactions, I→III→IV, but suggests that the dithiocarbamate function in III somewhat participates in the second substitution process, III→IV.

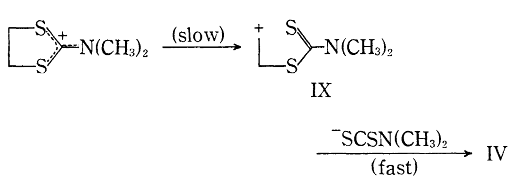
The Reaction of the Dithiolanylium Ion (V) with the Dithiocarbamate Anion (II). Winstein and co-workers have reported that the acetolysis of *trans*-2-acetoxycyclohexyl brosylate was about 630 times faster than that of the *cis*-isomer. This was interpreted by anchimeric assistance of the neighboring acetoxy group through the presumed acetoxonium ion.[8] Later the cation was isolated as the tetrafluoroborate *via* another route.[9] The dithiolanylium ion (V) isolated in the present work corresponds to the anchimeric acetoxonium ion. Thus, the reaction of the dithiolanylium perchlorate (Vb) with the dithiocarbamate anion was carried out first.

The perchlorate Vb was allowed to react with the dithiocarbamate salt (II) at 50°C in DMF to result in the quantitative formation of ethylene bis(dithiocarbamate) (IV). Possible mechanism for the formation of IV may be considered as follows:

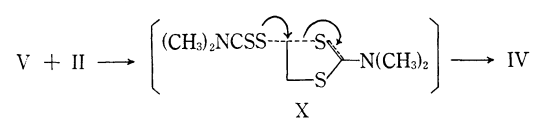
Mechanism A



Mechanism B

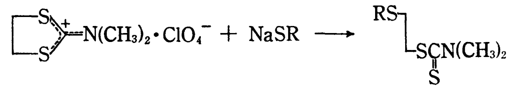


Mechanism C



Mechanism A involves initial addition of the anion at the position of lowest electron density, *i. e.*, the centered carbon (sp^2) atom of V to afford the adduct VIII followed by rearrangement to the product IV. Mechanism B consists of initial conversion of the stabilized carbonium ion V into the unstable ion IX which rapidly reacts with the anion to give IV (S_N1 type), while mechanism C involves attack of the anion at the neutral carbon (sp^3) atom of the position 4 in V through the transition state X (S_N2 type).

Firstly mechanism A can be eliminated by our observation that the perchlorate Vc also reacts with mercaptides incapable of rearrangement to result in the formation of β-mercaptoethyl dithiocarbamates (XI).



$R=C_2H_5$, p-$CH_3C_6H_4$ XI

Kinetic experiments indicate that the reaction of Vc with II fits in a second-order rate equation with respect to both reactants. The fact excludes mechanism B which should fit in a first-order rate equation. In conclusion, the dithiocarbamate anion attacks the C-4 atom to give IV through a concerted S_N2 type mechanism (mechanism C). The Arrehnius plots for the reaction in DMF is shown in Fig. 2. Activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$, were 23.0 kcal/mol and +3.7 *e.u.*, respectively.

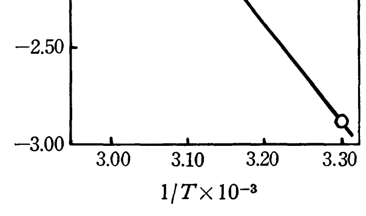


Fig. 2. The Arrehnius plot for the reaction of Vb with II in DMF.

Reaction Scheme. From results obtained, the formation of IV can be interpreted by the following scheme involving the intermediacy of the isolated anchimeric cation V.

Dichloride I reacts with II initially to give the monosubstituted III followed by rapid cyclization to the stable carbonium ion V. The carbonium ion further reacts with II to afford the disubstituted product (IV). The alternative formation of IV arising from the direct reaction of III with II not

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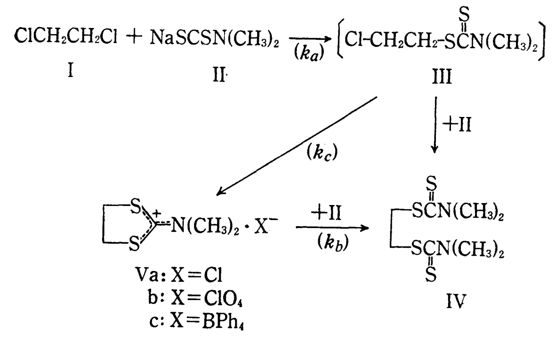
[8] For example, a) S. Winstein and R. E. Buckles, *J. Amer. Chem. Soc.*, **64**, 2780 (1942); b) S. Winstein, E. Grunwald and R. E. Buckles, *ibid.*, **70**, 816 (1948); c) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

[9] C. B. Anderson, E. C. Friedrich and S. Winstein, *Tetrahedron Lett.*, **1963**, 2037.



via Va might be neglected since the cyclization was rapid ($k_c \gg k_a$). In short, steps kinetically determining the product ratio are the process I→III (k_a) and Va→VI (k_b). It is expected that the rate of each product-determining process will be differently affected by the nature of the solvent used, and that the solvent effects on each process will be reflected in the product ratio.

The Neighboring-group Participation of the Dithiocarbamate Function. The rates (k_a) of the reaction I→III were obtained from those of reactions of *n*-butyl chloride with the dithiocarbamate ion. The rates (k_b) of the reaction Va (unisolatable)→IV were obtained from those for the reaction Vb→IV. The reactions were followed by determining the amount of the unreacted dithiocarbamate anion after given intervals. Kinetic experiments were carried out at 60°C in ethanol, DMF and dioxane, which represent dipolar protic dipolar aprotic and nonpolar aprotic solvent, respectively.

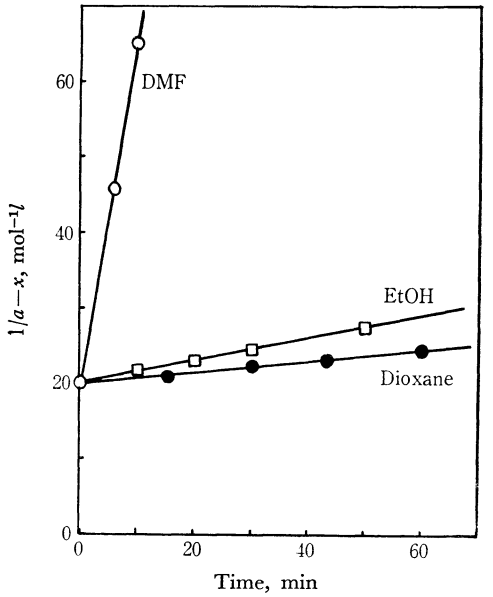


Fig. 3. The second-order rate plots for the reactions of *n*-butyl chloride with sodium *N*,*N*-dimethyldithiocarbamate:
The initial concn. = 0.050 mol/*l*

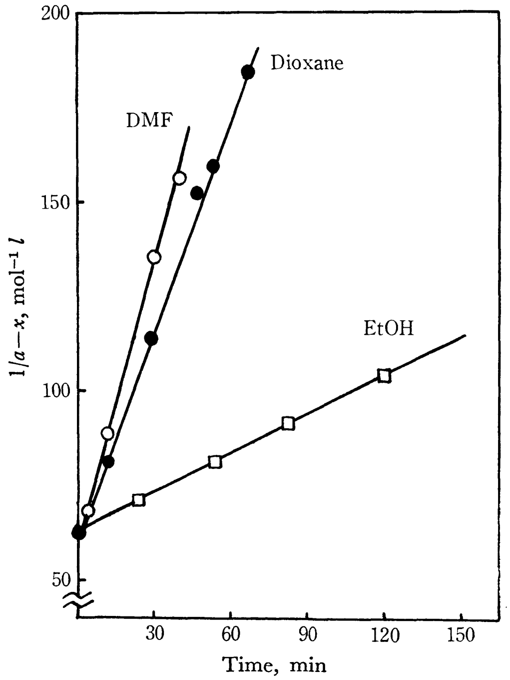


Fig. 4. The second-order rate plots for the reactions of Vb with sodium *N*,*N*-dimethyldithiocarbamate. The initial concn. = 0.0162 mol/*l*

Second-order rate plots for the equimolar reactions with II of *n*-butyl chloride and 2-dimethylamino-1,3-dithiolanylium perchlorate (Vb) in various solvents are shown in Figs. 3 and 4, respectively. Rate constants obtained for both reactions are summarized in Table 2.

Table 2. Rate constants for equimolar reaction with II of *n*-butyl chloride (k_a') and the perchlorate Vb (k_b') (60°C)

Solvent (Dielectric constant)	$10^3k_a'$	$10^3k_b'$	k_b'/k_a'	Product ratio* IV/V
	(l mol^{-1}sec^{-1})			
EtOH (24.3)	0.4	7.34	18.4	0.092
DMF (36.7)	70.8	40.9	0.58	0.30
Dioxane (2.2)	0.3	34.0	113	1.32

* A more accurate product ratio for the equimolar reaction of I with II could be calculated from IV%/(100-IV%) in Table 1 as it is difficult to isolate Va quantitatively.

In conclusion, the rate of the first process (k'_a) was in the order: dioxane≈EtOH≪DMF, while that of the second (k'_b) was in the order: EtOH≪dioxane<DMF. It is interesting to note that k'_a for DMF is very large, and that k'_b/k'_a for dioxane is significantly large, compared with those for EtOH and DMF. The unusual rate enhancement in DMF for the reaction of *n*-butyl chloride with II can be attributed to two major factors;

(i) the enhanced nucleophilicity of the dithiocarbamate anion with DMF, which is in agreement with many other observations for the S_N reactions in dipolar aprotic media[10] and (ii) the enhanced electrophilicity of the alkyl chloride due to the complex formation between the alkyl chloride and DMF molecules.[11] The rate enhancement in dioxane for the reaction of carbonium ion V with the anion can be explained by the consideration that the rate of the reaction between a cation and an anion increases with the decrease of the ionization power of the solvent since activation in such reaction requires partial neutralization of charge.[12]

Most important is the fact that in dioxane the second displacement reaction V→IV is about one hundred times faster than the first I→III, which might account for the more favorable formation of the disubstituted product (IV) in the equimolar reaction of I with II. This also led to the conclusion that participation of the neighboring dithiocarbamate function in III may be involved in the second substitution process III→IV, together with the solvent effect on the product ratio described above. In other words, dichloride I reacts with anion II to form the monosubstituted intermediate (III), which further reacts with II more readily to result in the favorable formation of the disubstituted product (IV) through the intermediacy of the isolated anchimeric cation V.

Neighboring-group participation*4 ($k'_b/k'_a>1$) was also observed in the reaction in ethanol, but less predominant than in dioxane. In DMF, the participation was not kinetically observed ($k'_b/k'_a<1$). Consequently IV may be also formed from the direct reaction of III with II not *via* V.

From the results, the relationship between rate data for each product-determining steps and the product ratio is summarized with respect to the nature of the solvent in Table 3.

TABLE 3. RATE DATA AND THE PRODUCT RATIO

Solvent	Rate of the process I→III		V→IV	Product ratio IV/V
Dipolar protic	slow	$<$	slow	small
Dipolar aprotic	fast	$>$	fast	medium
Nonpolar aprotic	slow	$\ll$	fast	large

In dipolar protic and aprotic solvents, rate difference between two kinetically product-determiing steps was not so large. In nonpolar aprotic solvents, the rate difference is significantly large and consequently neighboring-group participation of the dithiocarbamate function is more predominant. This is reflected in the favorable formation of the disubstituted product (IV) in the equimolar reaction of I with II.

Such participation of the dithiocarbamate function can account for the observation that, in equimolar reactions of α,ω-dichloroalkanes with the dithiocarbamate anion (II) in ethanol, the yield of the corresponding alkylene bis(dithiocarbamate) increases in the order: 1,4-dichlorobutane>1, 3-dichloropropane>1, 2-dichloroethane, indicating that such participation increases in the same order.[13] This fact also suggests that the rate of reaction of the corresponding anchimeric carbonium ion with II increases in the same order, which has been verified.[14] Furthermore, kinetical evidence that neighboring-group participation of this function is involved in the polymer reaction of poly(vinyl chloride) with sodium *N,N*,-diethyldithiocarbamate in DMF and THF has been obtained.[15]

Experimental*5

Equimolar Reactions of 1,2-Dichloroethane (I) with Sodium *N,N*-Dimethyldithiocarbamate (II) in Various Solvents. Into a solution of I (19.8 g, 0.20 mol) in 80 m*l* of the solvent was added a solution of sodium *N,N*-dimethyldithiocarbamate hydrate (II)*6

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[10] For reviews on the subject, see A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962); "Advances in Physical Organic Chemistry," Vol. 5, ed. by V. Gold, Academic Press Inc., New York (1967), p. 173.

[11] a) S. Yoneda, I. Morishima, K. Fukui and Z. Yoshida, *Kogyo Kagaku Zasshi*, **68**, 1074 (1965); b) S. Yoneda, Z. Yoshida, I. Morishima and K. Fukui, *ibid.*, **68**, 1077 (1965).

[12] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt Co., Inc., New York (1959), p. 259.

*4 Neighboring-group participation in the present work might be considered to be essentially the same as the "anchimeric assistance" proposed by Winstein[8] for solvolytic (S_N1) reactions. The phenomenon in which the cyclic compound is formed by participation of the neighboring group is called "anchimerism,"[13] and was used in a preliminary communication of this work.*1 However, this term is not appropriate for our present observation since it does not mean rate enhancement by a neighboring group.

[13] a) F. L. Scott and D. F. Fenton, *Tetrahedron Lett.*, **1964**, 1681; b) F. L. Scott and E. Flynn, *ibid.*, **1964**, 1675.

[14] T. Nakai, Y. Ueno and M. Okawara, Abstracts of papers presented at the 18th Symposium on Organic Reaction Mechanisms, Kyoto, October, 1967, p. 77.

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

*5 All melting and boiling points were uncorrected. Infrared and ultraviolet spectra were recorded on Hitachi infrared EPI-S2 and recording EPS-2 spectrophotometers, respectively. The NMR spectrum was obtained with a Varian Associates Model A-60 spectrometer in a dimethylsulfoxide-d_6 solution using tetramethylsilane as an internal standard.

*6 The dithiocarbamate salt contains two molecules of the coordinated water: T. Nakai and M. Okawara, This Bulletin, **41**, 707 (1968).

(36.0 g, 0.20 mol) in 120 m*l* of the solvent. The reaction mixture was stirred at 60°C for 6 hr in nitrogen atmosphere. Sodium chloride formed was filtered off and the filtrate was concentrated in reduced pressure. The mixture was poured into 300 m*l* of cold water to give a white precipitate, ethylene bis(*N*,*N*-dimethyldithiocarbamate) (IV), which was filtered, dried *in vacuo* and weighed; mp 187—189°C (lit,[16] 189°C); IR (KBr): $\nu_{C=N(thioureide)}$[17] 1495 cm^{-1}; UV: λ_{max}^{EtOH} 250, 277 mμ.

A portion of the filtrate was treated with an excess of an aqueous solution of nickel chloride to produce no precipitate of the nickel salt, indicating that the dithiocarbamate anion completely disappeared during reaction. The filtrate was extracted with ether. A given volume of the aqueous layer was treated with an excess of an aqueous solution of sodium perchlorate to give a white precipitate, 2-dimethylamino-1,3-dithiolanylium perchlorate (Vb), which was then filtered, dried *in vacuo* and weighed; mp 179—181°C (recrystalized from acetone); UV: $\lambda_{max}^{H_2O}$ 249 mμ (ε=13000). The NMR spectrum shows two singlet signals at δ 4.08(2H) and 3.62 ppm (3H) (Fig. 1).

Found: C, 24.48; H, 4.18; N, 5.58%. Calcd for $C_5H_{10}ClNO_4S_2$: C, 24.24; H, 4.08; N, 5.66%.

A given volume of the aqueous layer was treated with an excess of an aqueous solution of sodium tetraphenylborate to afford a white precipitate, the dithiolanylium tetraphenylborate (Vc), which was filtered, dried *in vacuo* and then weighed; mp 134—136°C (recrystallized from acetonitrile).

Found: C, 74.81; H, 6.50; N, 3.22%. Calcd for $C_{29}H_{40}BNS_2$: C, 74.51; H, 6.47; N, 3.00%.

Authentic 2-dimethylamino-1,3-dithiolanylium salts were prepared by treating β-hydroxyethyl *N*,*N*-dimethyldithiocarbamate with *p*-toluenesulfonyl chloride in DMF[6] followed by sodium perchlorate or sodium tetraphenylborate.

The ethereal layer was dried over anhydrous sodium sulfate and the solvent was removed *in vacuo* to give a small amount of yellow oily residue. The infrared spectrum (liq. film) showed a strong absorption band at 1650 cm^{-1} due to -S-CO-N<. In the case of the reaction in ethanol, the oily residue was distilled in the reduced pressure to give ethyl *N*,*N*-dimethylthioncarbamate (VI) and β-mercaptoethyl *N*,*N*-dimethylthiolcarbamate (VII) in 5.5% and 3.9% yield, respectively. Physical properties of product VI are as follows: bp 81—82°C/10 mmHg (lit,[18] 82.6°C/10 mmHg); $n_D^{25°C}$ 1.5082 (lit,[19] $n_D^{20°C}$ 1.5075); UV: λ_{max}^{EtOH} 250.5, 285 mμ (lit,[20] 250.5, 285 mμ). Thioncarbamate (VI) was transformed with ethyl bromide into thiolcarbamate,[21] which was identified by means of spectral and physical data with the authentic compound. The physical data for thiolcarbamate (VII) are as follows: bp 112—117°C/4 mmHg; $n_D^{25°C}$ 1.5840; IR (neat): 1650, 1495 cm^{-1} (-S-CO-N<). The product was treated with a mercuric chloride solution to give a precipitate of the mercury mercaptide: mp 122—128°C; IR (KBr): $\nu_{C=O}$ 1635 cm^{-1}, and was oxidized to disulfide: mp 83—84°C (recrystallized from cyclohexane); IR (KBr): $\nu_{C=O}$ 1640 cm^{-1}.

Found: N, 8.10%. Calcd for $C_{10}H_{20}N_2O_4S_4$: N, 8.54%.

Product compositions obtained from the equimolar reactions in various solvents are shown in Table 1.

Reaction of 2-Dimethylamino-1,3-dithiolanylium Perchlorate (Vb) with Sodium *N*,*N*-Dimethyldithiocarbamate (II). A mixture of 2.5 g (0.01 mol) of perchlorate and 2.0 g (0.01 mol) of sodium salt in 20 m*l* of DMF was stirred at 60°C for 4 hr. The mixture was poured into a large amount of cold water to produce 2.6 g (98%) of a white precipitate: mp 187—189°C (recrystallized from DMF). The precipitate showed no depression upon a mixed mp determination with the authentic ethylene bis(*N*,*N*-dimethyldithiocarbamate) (IV), and its infrared spectrum was in complete agreement with that of the authentic sample.

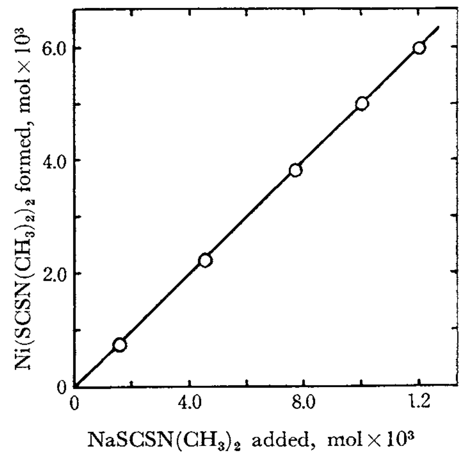

Fig. 5. The calibration curve for the determination of the dithiocarbamate anion.

Kinetic Runs. The rates of both reactions of *n*-butyl chloride and 2-dimethylamino-1,3-dithiolanylium perchlorate (Vb) with sodium *N*,*N*-dimethyldithiocarbamate were followed by measuring quantities of the unreacted dithiocarbamate anion after given intervals. The dithiocarbamate anion was gravimetrically determined from the quantity of the nickel chelate precipitated by treating an aqueous layer of the sample with an excess of an aqueous solution of nickel chloride. An exampe of the calibration curve is shown in Fig. 5. All reactions were carried out at 60°C under equimolar conditions.

TABLE 4. REACTIONS OF *n*-BUTYL CHLORIDE WITH II IN ETHANOL

Time, min	Ni-saklt formed, g	1/*a*—*x*, mol^{-1}*l*
10	0.2755	21.7
20	0.2717	22.0
30	0.2608	22.9
50	0.2630	22.7

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[16] A. W. Campbell and P. F. Tryan, *Ind. Eng. Chem.*, **45**, 125 (1953).

[17] H. M. Randall, R. G. Fowler, N. Fuson and J. Dangl, "Infra-red Determination of Organic Structure," Van Nostrand, New York (1949).

[18] O. Biffeter, *Ber.*, **43**, 1853 (1910).

[19] B. Holmberg, *Svensk. Kem. Tids.*, **41**, 249 (1929).

[20] M. J. Janssen, *Rec. Trav. Chim. Pays-Bas*, **79**, 454, 464 (1960).

[21] A. F. Schöberl and A. Wagner, "Houben-Wyle: Methoden der Organischen Chemie," Vol. IX, George Thieme Verlag, Stuttgart (1955), p. 837.

Initial concentrations for reactions of *n*-butyl chloride and the dithiolanylium perchlorate were 0.050 and 0.016 mol/*l*, respectively.

n-Butyl chloride (0.5785 g) was dissolved in a solution of 1.1650 g of sodium *N*,*N*-dimethyldithiocarbamate in 125 m*l* of the solvent placed in a constant-temperature bath at 60±0.2°C. At various intervals a 25.0-m*l* aliquot of the yellow solution was removed and poured into cold water (*ca.* 50 m*l*). The sample solution was immediately extracted with ether, then the aqueous solution was treated with an excess of an aqueous solution of nickel chloride giving green precipitates of nickel chelate. The nickel chelate was collected in a glass filter which had been weighed. The glass filter was dried *in vacuo*. An example of results is given in Table 4. All plots of $1/a-x$ against time showed straight lines (Fig. 3).

2-Dimethylamino-1,3-dithiolanylium perchlorate (Vb) (1.000 g) was dissolved in a solution of 0.725 g of sodium *N*,*N*-dimethyldithiocarbamate in 150 m*l* of the solvent. At various intervals a 50.0-m*l* aliquot was removed and poured into cold water (*ca.* 100 m*l*) giving white precipitates of ethylene bis(*N*,*N*-dimethyldithiocarbamate) (IV). The precipitates were filtered off and the aqueous layer was treated with an excess of an aqueous solution of nickel chloride giving green precipitates of the nickel chelate. The quantity of the nickel chelate was measured as in the case of the reaction of *n*-butyl chloride with II. An example of results is shown in Table 5. All plots of $1/a-x$ against time showed straight lines (Fig. 4).

TABLE 5. REACTIONS OF Vb WITH II IN DMF

Time, min	Ni-salt formed, g	$1/a-x$, mol^{-1}l
5	0.1135	66.4
12	0.0840	88.9
30	0.0550	136
40	0.0445	157