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Tri(hetero)substituted Carbonium Ions. VI. An Anomalous Reaction of 2-Methylthio-1,3-dithiolanylium Ion with *N,N*-Dimethyldithiocarbamate Anion[*1]

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The reaction of 2-methylthio-1,3-dithiolanylium ion (III) with *N,N*-dimethyldithiocarbamate anion ($^{-}$SN) has been studied with a view toward demonstrating the ambident character of the cation III. It was found that (i) the reaction afforded *S*-*β*-(*N,N*-dimethyldithiocarbamyl)ethyl-S′-methyltrithiocarbonate (IV; normal) together with ethylene bis(*N,N*-dimethyldithiocarbamate) (V; abnormal); (ii) methylthioxanthate anion ($^{-}$SS) was formed in the reaction; (iii) the formation of the abnormal product (V) was more favorable and this could not be ascribed to the attack of $^{-}$SN on the normal product (IV). The ambident reactivity of cation III has been compared with that of closely related cations, tris(methylthio)carbonium ion and 2-methylamino-1,3-dithiolanylium ion (Ia). It was also found that the reaction of Ia with ethylthioxanthate anion ($^{-}$SS′) afforded the *S*′-ethyl analog of IV (normal) together with a small amount of abnormal V. The mechanism for the formation of the abnormal product (V) both from III and $^{-}$SN and from Ia and $^{-}$SS′ has been suggested.

In previous papers[1–5] we reported that various dithiocarbamidium ions including 2-dialkylamino-

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[*1] Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

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

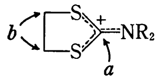
2) T. Nakai and M. Okawara, *Tetrahedron Lett.*, **1967**, 3835; This Bulletin, **43**, 1864 (1970).

3) T. Nakai, Y. Ueno and M. Okawara, This Bulletin, **43**, 3175 (1970).

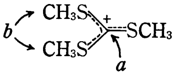
4) T. Nakai and M. Okawara, the 20th Annual Meeting of the Chemical Society of Japan, Tokyo. April, 1967; This Bulletin, **43**, 3528 (1970).

5) T. Nakai, K. Hiratani and M. Okawara, This Bulletin, **43**, 3016 (1970).

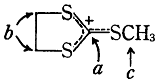
1,3-dithiolanylium ions (I) are ambident electrophiles capable of undergoing reactions with nucleophiles at two sites *a* and *b* in formula (I). Recently Tucker and Roof reported a similar behavior of tris(methylthio)carbonium ion (II).[6] However, little information on the ambident behavior of a cyclic analog of II, 2-methylthio-1,3-dithiolanylium ion (III), has can be found in literature, although reactions at the central carbon atom (site *a*) of III have been reported.[7]



I



II



III

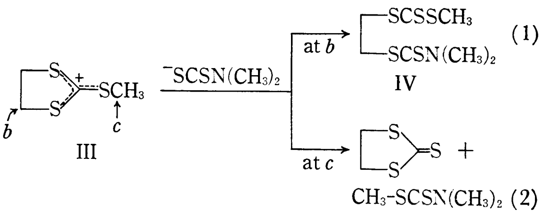
The purpose of this work is to demonstrate that cation III is also capable of undergoing electrophilic reactions at sites *b* or *c*. It has been established with some exceptions that cation I directs the attack of polarizable or bulky nucleophiles to site *b* and the attack of basic nucleophiles to site *a*.[2] Thus the reaction of III with *N*,*N*-dimethyldithiocarbamate anion, ranked as one of the most polarizable nucleophiles,[8] has been studied in detail.

In this paper anomalous results on the reaction of III with the dithiocarbamate anion are presented and the electrophilic reactivity of III is compared with that of closely related carbonium ions I and II.

Results

Isolation of Cation III as Perchlorate. Recently Gompper and Kutter[7] reported the formation of the methyl sulfate salt of III from the reaction of ethylene trithiocarbonate with dimethyl sulfate. However, the salt was not isolated. In this study, cation III was isolated as perchlorate (IIIa) in 72% yield by treatment of the methyl sulfate salt with an aqueous solution of sodium perchlorate. Recrystallization of the perchlorate from acetone gave colorless needles melting at 101—102°C. The NMR spectrum of IIIa showed two singlet signals at δ 3.21(CH_3S) and 4.37 ppm (CH_2S).

Reactions of 2-Methylthio-1,3-dithiolanylium Ion with *N*,*N*-Dimethyldithiocarbamate Anion. If we assume that III reacts with the dithiocarbamate anion in the same manner as cation I,[1,2] the reaction can be expected to yield *S*-β-(*N*,*N*-dimethyldithiocarbamyl)ethyl-*S'*-methyltrithiocarbonate(IV) as the sole product (Eq. (1)). There is another possibility that III and the dithiocarbamate anion would afford ethylene trithiocarbonate and methyl dithiocarbamate (Eq. (2)), if III behaves in the same manner as 2-methylthio-3-methyl-4,5-dihydrothiazolium ion.[9]



Thus the reaction of IIIa with sodium *N*,*N*-dimethyldithiocarbamate (abbreviated as NaSN) was carried out under various conditions. It was found that the reaction of III with NaSN gave ethylene bis(*N*,*N*-dimethyldithiocarbamate) (V) as a major product together with a very small amount of expected product IV. Bis(dithiocarbamate) V was identified by comparison of the IR and UV spectra with those of the authentic sample. Identification of product IV will be described below.

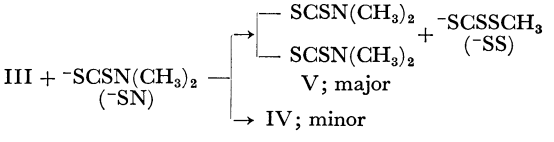
Table 1 shows yields of the unexpected product (V) under various conditions indicating that the yield of V increases either with reaction time or with an increase in the amount of NaSN employed. As a matter of course the formation of unexpected V must be accompanied by the elimination of thioxanthate moiety ($SCSSCH_3$) (abbreviated as SS) from cation III.

Table 1. Reaction of IIIa with NaSN

Run	IIIa mmol	NaSN mmol	DMF m*l*	Temp. °C	Time hr	Bis (dithiocarbamate) (V), Yield,[a] %
1	10	10	20	55	4	26
2	20	20	25	60	7	52
3	10	20	25	60	6	69
4	10	28	25	40	6	71

a) Based on IIIa

In order to prove occurrence of the elimination of the thioxanthate moiety, the UV spectrum of an aqueous solution of the resulting mixture was measured (Fig. 1). Comparison of this spectrum with that of NaSN and sodium ethylthioxanthate (NaSS') suggested that the aqueous solution contained both methylthioxanthate and unreacted dithiocarbamate anions.



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[6] W. P. Tucker and G. L. Roof, *Tetrahedron Lett.*, **1967**, 2747; *J. Org. Chem.*, **33**, 3333 (1968).

[7] R. Gompper and E. Kutter, *Angew. Chem. Int. Ed. Engl.*, **2**, 687 (1963); *Chem. Ber.*, **98**, 1365, 1374 (1965).

[8] R. E. Davis, "Survey of Progerss in Chemistry," Vol. 2, ed. by A. Scott, Academic Press Inc., New York, N. Y. (1964), p. 189; R. E. Davis, H. Nakshbendi and A. Ohno, *J. Org. Chem.*, **31**, 2702 (1966).

[9] T. Nakai, K. Hiratani and M. Okawara, the 19th Symposium on Organic Reaction Mechanisms, Yamagata, October, 1968; This Bulletin, to be published.

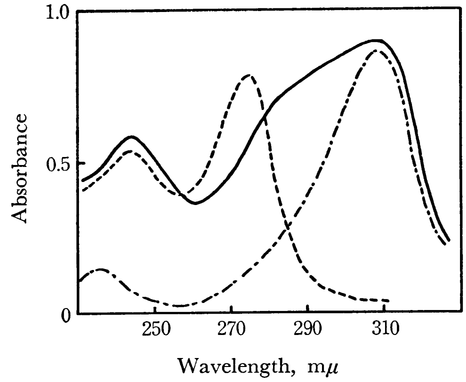


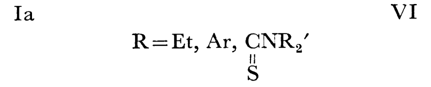
Fig. 1. UV spectra of the resulting aqueous solution (————), sodium *N*,*N*-dimethyldithiocarbamate (---------; ε_{max} (281 mμ) 12200) and sodium ethylthioxanthate (–·–·–·; ε_{max} (335 mμ) 9300) in water.

The molar ratio of $^{-}$SS to $^{-}$SN remaining in the aqueous solution was calculated from absorbances at 281 and 335 mμ on the assumption that the molar extinction coefficient (ε) of $^{-}$SS is the same as that of $^{-}$SS'. It was found in the case of Run 3 that the molar ratio was 0.90 and, hence, 7.5 mmol of $^{-}$SN remained unreacted since the molar amount of $^{-}$SS eliminated should be the same as that of bis(dithiocarbamate) (V) formed (Table 2). The finding indicates that most of reacted $^{-}$SN is distributed in the unexpected product (V).

TABLE 2. THE DISTRIBUTION OF SN MOIETY (RUN 3)

Before the reaction -SN (mmol)	After the reaction (mmol)		
	V	Unreacted -SN	($^{-}$SS)
20.0	13.8±2.0	7.5±1.0	(6.9±1.0)

Reaction of 2-Dimethylamino-1,3-dithiolanylium Ion with Ethylthioxanthate Anion. As has been shown,[1,2] 2-dimethylamino-1,3-dithiolanylium ion (Ia) reacts with sulfur nucleophiles to give the open-chain products (VI).



R=Et, Ar, CNR$_2$' (C=S)

In view of the separate preparation of the *S*'-ethyl analog (IV') of the minor product (IV) obtained above, the reaction of the cation Ia with sodium ethylthioxanthate (NaSS') was carried out. However, contrany to our expectation, it was found that Ia and $^{-}$SS' gave an abnormal product, bis(dithiocarbamate) (V), in low yields along with the normal product (IV') as the main product.

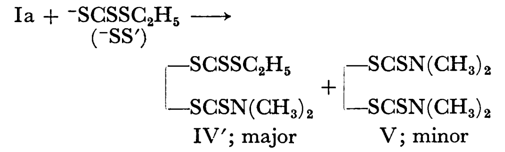


TABLE 3. REACTIONS OF Ia WITH NaSS'

Ia mmol	NaSS' mmol	DMF ml	Temp. °C	Time hr	Yields[a)] (%) of products	
					IV'	V
20.0	30.0	25	70	6	37.0	5.5
50.0	50.0	40	60	6	22.0	0.7

a) Based on Ia

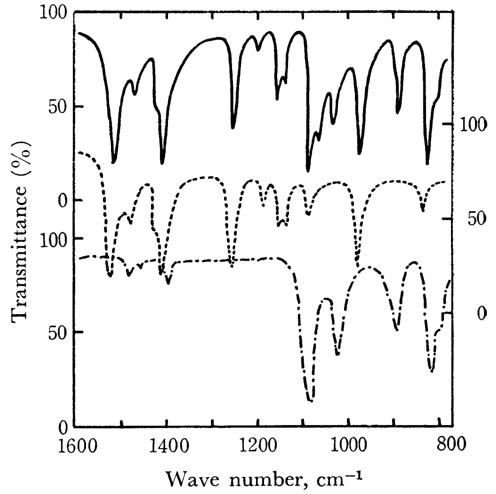


Fig. 2. IR spectra of product IV' (neat; ————), bis(dithiocarbamate) V (KBr disk; ---------) and *S*,*S*'-diethyltrithiocarbonate (neat; –·–·–·).

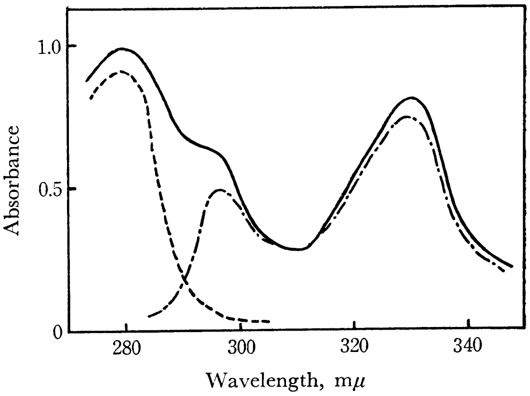
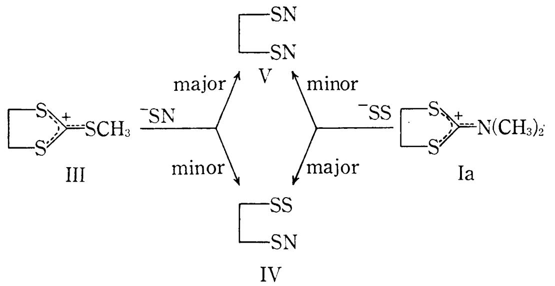


Fig. 3. UV spectra of product IV' (————), *S*-ethyl *N*,*N*-dimethyldithiocarbamate (---------) and *S*,*S*'-diethyltrithiocarbonate (–·–·–·) in ethanol.

Product IV' (a yellowish liquid) was purified by means of column chromatography on alumina and identified by IR and UV spectra, which are shown in Figs. 2 and 3 together with those of related compounds. It is apparent from these spectra that the product IV′ has both –S–CS–N< and –S–CS–S– moieties. The IR and UV spectra of the minor product (IV) obtained from III and $^-$SN were essentially identical with those of IV′.

Discussion

The Ambident Character of Cation III. The above results are summarized in the following scheme.



[SN=SCSN(CH$_3$)$_2$; SS=SCSSR′ (R′=CH$_3$ or C$_2$H$_5$)]

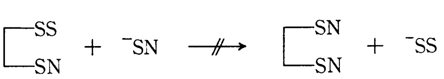
The normal product (IV) from III and $^-$SN is best explained as the result of the attack of $^-$SN on the *S*-methylene carbon atom (site *b*) of III presumably through the S$_N$2-like mechanism which has been accepted for the reactions of Ia with sulfur nucleophiles.1,3) The combined results of the present work and that by Gompper and Kutter7) reveal that cation III is an ambident electrophile with reactive sites at the central carbon (*sp*^{2}) and the *S*-methylene carbon (*sp*^{3}) atoms, although the mechanism of the formation of V remains unsettled.

The following evidence indicates that the *S*-methylene carbon atom of III is less reactive than that of Ia. Ia reacts with *p*-tolylmercaptide ion at 60°C giving VI (R=*p*-CH$_3$C$_6$H$_4$) in 77% yield,2) while III does not react with the mercaptide ion under the same conditions. The smaller reactivity of III seems surprising because it would be more destabilized than Ia since the 2-SMe group in III is less electron-donating than the 2-NMe group in Ia.

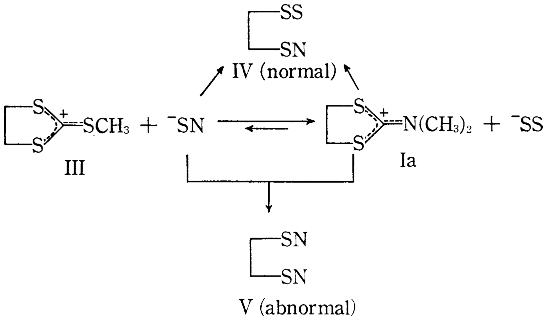
Let us compare the electrophilic reactivities of cation III and its open-chain analog, tris(methylthio)carbonium ion (II). It has been established that the five membered cation Ia is more stabilized than its open-chain analog of Ia.3,4) By analogy, it is believed that III is more stabilized (less electrophilic) than open-chain II. The following evidence indicates smaller reactivity of III; as decribed above, III does not react with $^-$SC$_6$H$_4$CH$_3$ at any sites under given conditions, whereas II is capable of undergoing reaction with a less nucleophilic mercaptide ion ($^-$SCH$_3$) at the central carbon atom (site *a*) to afford tetrakis(methylthio)methane.6)

On the Mechanism of Formation of the Abnormal Product (V). Let us consider the mechanism of the formation of the abnormal product from III and $^-$SN. Another formation of V from Ia and $^-$SS′ would take place by the subsequent reaction of $^-$SN eliminated from Ia with another molecule of Ia.

Controlled experiments demonstrated that neither *S,S*′-dimethyltrithiocarbonate nor trithiocarbonate IV′ reacted with $^-$SN at all. The result undoubtedly eliminated the possibility that the formation of the abnormal product (V) took place by the attack $^-$SN on the normal product (IV). This also indicates that the formation of V is competition with the formation of IV in both cases.



Thus, in order to explain the results, we have assumed the following scheme involving a direct interconversion between III and Ia.

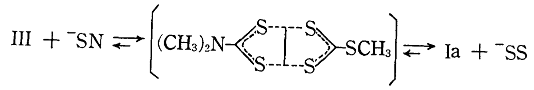


In the above scheme it has been established that (i) the *S*-methylene carbon atom of Ia is more electrophilic than that of III; (ii) $^-$SN is much more nucleophilic than $^-$SS;9) (iii) Ia reacts preferentially with $^-$SN to afford bis(dithiocarbamate) V. From the scheme, the abnormal product (V) from III and $^-$SN is best explained as the result of an initial transformation of III with $^-$SN into Ia which then preferentially reacts with another molecule of $^-$SN, finally yielding V. Similarly V from Ia and $^-$SS′ is explained as the result of capturing $^-$SN formed *via* the interconversion process with another molecule of Ia.

The scheme may also account for both favorable formation of abnormal V from III and $^-$SN and favorable formation of normal IV′ from Ia and $^-$SS′; the more reactive cation Ia directs the attack of $^-$SS preferentially to the formation of IV, whereas the less reactive cation III reacts with $^-$SN preferentially to give cation Ia, finally yielding V.

As a result, in the absence of data to the contrary, it seems reasonable to assume the above scheme for the formation of V and for the elimination of ^-SS from III with ^-SN.

Finally, the problem concerning the mechanism of the interconversion: III$+^-$SN$\rightleftarrows$Ia$+^-$SS, still remains. Although the accurate mechanism of the interconversion process is not elucidated as yet, the following two-centered substitution might be assumed as a possible mechanism. However, its confirmation needs further studies.



Experimental

Melting points are uncorrected. The IR and UV spectra were recorded with Hitachi EPI-S2 and EPS-2 spectrometers, respectively. The NMR spectrum of perchlorate IIIa was obtained on a Varian Associate A-60 spectrometer in a $(CD_3)_2SO$ solution using tetramethylsilane as an internal standard.

Materials. *Sodium N,N-dimethyldithiocarbamate.* A commercial product was washed with chloroform before use.

Sodium ethylthioxanthate was prepared, from sodium ethylmercaptide and carbon disulfide according to Barltrop *et al.*[10]

2-Dimethylamino-1,3-dithiolanylium perchlorate (Ia) was prepared by the method[2] given previously. mp 179—180°C (acetone).

Ethylene trithiocarbonate. A commercial product was purified by recrystallization before use.

Preparation of 2-Methylthio-1,3-dithiolanylium Perchlorate (IIIa). Ethylene trithiocarbonate (27.2 g, 0.02 mol) was dissolved in 25.2 g (0.02 mol) of dimethyl sulfate. When the mixture was heated to 50°C a vigorous exothermic reaction occurred. The reaction temperature was kept below 90°C. After the exothermic reaction ceased, the mixture was further stirred at 95°C for 30 min. On cooling the mixture was poured into 200 m*l* of a saturated aqueous solution of sodium perchlorate giving 35.8 g (72%) of pale yellowish precipitates. The precipitates were washed with ether and recrystallized from acetone giving colorless needles: mp 101—102°C.

Found: C, 18.84; H, 2.93%. Calcd for $C_4H_7ClO_4S_3$: C, 19.16; H, 2.82%.

Reactions of 2-Methylthio-1,3-dithiolanylium Perchlorate (IIIa) with Sodium *N,N*-Dimethyldithiocarbamate (NaSN). A typical run is as follows. Carbonium salt IIIa (2.50 g, 0.02 mol) and NaSN (3.60 g, 0.02 mol) were dissolved in 20 m*l* of DMF. The mixture was stirred at 60°C for 6 hr, then poured into 150 m*l* of cold water giving precipitates of ethylene bis(*N,N*-dimethyldithiocarbamate) (V). The precipitates were filtered and washed with ether: mp 188—189°C (DMF) (188—190°C[11]).

The IR spectrum of the product was in agreement with that of the authentic sample.

The filtrate was extracted with ether. The ethereal layer was dried over anhydrous sodium sulfate and the solvent evaporated under reduced pressure giving a small amount of a yellowish oil of *S*-*β*-(*N,N*-dimethyldithiocarbamyl)ethyl-*S'*-methyltrithiocarbonate (IV). The IR and UV spectra of the oily residue were essentially identical with those of *S*-*β*-(*N,N*-dimethyldithiocarbamyl)ethyl-*S'*-ethyltrithiocarbonate (IV') described below.

The UV spectrum of the aqueous layer was measured (Fig. 1) indicating that the aqueous solution contained both thioxanthate and dithiocarbamate anions.

Reactions of 2-Dimethylamino-1,3-dithiolanylium Perchlorate(Ia) with Sodium Ethylthioxanthate (NaSS'). A typical run is as follows. Carbonium salt Ia (12.5 g, 0.05 mol) and NaSS' (8.0 g, 0.05 mol) were dissolved in 40 m*l* of DMF. The reaction mixture was stirred at 60°C for 6 hr. The mixture was poured into 300 m*l* of cold water giving 0.31 g of precipitates of V: mp 188—189°C (DMF) (188—190°C[11]). The IR spectrum of the product was identical with that of the authentic sample.

The filtrate was extracted with ether. Work-up gave 5.8 g of yellowish oil of *S*-*β*-(*N,N*-dimethyldithiocarbamyl)ethyl-*S'*-ethyltrithiocarbonate (IV'). Distillation of the oil *in vacuo* was unsuccessful. Thus the oil was purified by means of column chromatography on alumina: n_D (25°C) 1.6605.

Found: N, 4.79%. Calcd for $C_8H_{15}NS_5$: N, 4.91%.

The IR and UV spectra of the oily product are shown in Figs. 2 and 3, respectively.

The authors are greateful to Sanshin Chem. Ind. Co., Ltd., for the gift of ethylene trithiocarbonate and to Sankyo Co., Ltd., for measurement of the NMR spectrum.

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[10] J. A. Barltrop, P. M. Hayes and M. Calvin, *J. Amer. Chem. Soc.*, **76**, 4348 (1954).

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