BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1864—1869 (1970)

Tri(hetero)substituted Carbonium Ions. II. 2-Dialkylamino-1,3-dithiolanylium Ions. Reactions with Nucleophiles and Ambident Behaviors[1,2]

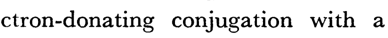
Takeshi NAKAI and Makoto OKAWARA

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

(Received January 17, 1970)

The reactions of 2-dialkylamino-1,3-dithiolanylium perchlorates with a variety of nucleophilic species including oxygen, sulfur and nitrogen nucleophiles have been investigated. Examination of the isolated products reveals that these trihetrosubstituted carbonium ions behave as ambident electrophiles toward nucleophiles with two reactive sites, *i.e.*, the electron-deficient centered carbon (a) and the ring-methylene carbon atom (b), and that the nature of nucleophiles greatly affects the reaction course in a straightforward manner. The reaction course may be classified as follows. If the nucleophile is basic, the reaction at the site (a) (mode A) is favored, but if it has large substituents, the initial proton abstraction reaction (mode C) is predominant, while if the nucleophile is polarizable, the reaction at the site (b) (mode B) is favored. The major factor deciding the reaction course is discussed in terms of the schematic energy profile of the overall reaction.

Stabilization of carbonium ions is usually done by electron-donating conjugation with a hetero atom adjacent to the electron-deficient carbon atom. Stabilization is more manifest when two or three electron-donating groups coordinate their nonbonding electron pairs with the cationic center.[3]



$$\ddot{\mathrm{X}}-\underset{:\mathrm{X}}{\overset{+}{\mathrm{C}}}-\ddot{\mathrm{X}} \longleftrightarrow \overset{+}{\mathrm{X}}{=}\underset{:\mathrm{X}}{\mathrm{C}}-\ddot{\mathrm{X}} \longleftrightarrow \textit{etc.}$$

X = S, N, O, Cl, *etc.*

Carbonium ions stabilized through two hetero atoms are of great significance from preparative and theoretical points of view, since they are readily isolated under an ordinary condition and behave toward nucleophiles as ambident electrophiles having two reactive sites.[4] Among them dialkoxycarbonium salts are the most important as facile alkylating agents.[5] However, very little systematic investigation has been carried out as regards carbonium ions stabilized through three α-hetero atoms although reactions of trialkoxy-[6] and trialkylthiocarbonium ions[7] have been reported.

In our previous paper[2] it was shown that 2-dimethylamino-1,3-dithiolanylium ion (Ia),[8] one of the carbonium ions substituted by one nitrogen and two sulfur atoms, is isolated as perchlorate or tetraphenylborate, and that Ia reacts with hydroxide and *N,N*-dimethyldithiocarbamate ions to give, respectively, β-mercaptoethyl *N, N*-dimethylthiolcarbamate and ethylene bis(*N,N*-dimethyldithiocarbamate). These observations suggest that Ia may behave as an ambident electrophile with two reactive sites, (a) and (b), as shown below.

---

1) T. Nakai and M. Okawara, *Tetrahedron Lett.*, **1967**, 3835. A preliminary communication.

2) Part I: T. Nakai, Y. Ueno and M. Okawara, This Bulletin, **43**, 156 (1970).

3) To what extent one is justified in considering such a cation a carbonium ion rather than an onium ion, depends upon the extent of contribution to the resonance hybrid of the structure carrying the positive charge on carbon and on the electron-donating tendency of the hetero atom X. Other factors, *e. g.*, steric ones which enhance or diminish the internal dissipation of charge, are also important: *cf.* C. D. Nenitzescu, "Carbonium Ions," ed. by G. A. Olah and P. von R. Schleyer, Vol. 1, Interscience Publ., New York, N. Y. (1968), p. 20. In our studies these cations are regarded as triheterosubstituted carbonium ions only for a systematic nomenclature.

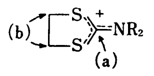
4) For a review, see S. Hünig, *Angew. Chem. Intern. Ed.*, **3**, 548 (1964).

5) S. Kabuss, *ibid.*, **5**, 675 (1966); K. Dimroth and D. Heinrich, *ibid.*, **5**, 676 (1966).

6) H. Meerwein, K. Bodenbenner, P. Borner, F. Kunnert and K. Wunderlich, *Ann. Chem.*, **632**, 38 (1960); H. Meerwein, V. Hederick, J. Morschel and K. Wunderlich, *ibid.*, **635**, 1 (1960); H. Meerwein, "Houben-Weyl: Methoden der Organischen Chemie," Vol. VI/3, Georg Thieme Verlag, Stuttgart (1965), p. 346.

7) R. Gompper and E. Kutter, *Chem. Ber.*, **98**, 1365 (1965); W. P. Tucker and G. L. Roof, *Tetrahedron Lett.*, **1967**, 2747.

8) This carbonium ion is more exactly termed 2-dimethylamino-1,3-dithiolan-2-ylium ion. In our papers the word 1,3-dithiolanylium is used only for the sake of convenience. The carbonium ion is also termed 2-dimethylamino-1,3-dithiolenium ion: J. L. Richards, D. S. Tarbell and E. H. Hoffmeister, *Tetrahedron*, **24**, 6485 (1968).



Ia, $R=CH_3$ b, $R=C_2H_5$

In general, the relative reactivities at the two reactive sites of such ambident electrophiles should depend upon three factors: the nature of the nucleophile, the structure of the carbonium ion, and the reaction conditions. Thus a systematic investigation of the effects of these factors on the reactivities of carbonium ions stabilized through one nitrogen and two sulfur atoms was initiated.

The present paper describes the effect of the nature of nucleophile on the reactivity and reaction course of 2-dialkylamino-1,3-dithiolanylium ions. The subsequent paper[9] is concerned with structural effect on reactivities of this type of ambident electrophiles.

Results and Discussion

2-Dialkylamino-1,3-dithiolanylium ions (Ia, $R=CH_3$; Ib, $R=C_2H_5$) were isolated as perchlorate from the equimolar reaction of 1,2-dichloroethane with the corresponding sodium *N*,*N*-dialkyldithiocarbamate in ethanol.[2] These carbonium salts were recrystallized from aqueous solutions. In order to investigate the effect of the nature of nucleophile on reactivities of these carbonium ions, reactions of I with a variety of nucleophilic reagents including oxygen nucleophilies (hydroxide and ethoxide), sulfur nucleophiles (alkyl and aryl mercaptides, and dithiocarbamates), nitrogen nucleophiles (anilines and triethylamine) and carbon nucleophile (cyanide) were studied.

A wide spectrum of reactivity is shown by 2-dialkylamino-1,3-dithiolanylium ions (Chart 1). Reaction conditions and products obtained are summarized in Table 1. Identification of products is based upon elemental analyses, physical properties, spectral data and chemical transformations (Experimental section),

It can be said, on the whole, that these two carbonium ions behave toward nucleophiles in a similar manner, although the dimethylamino compound (Ia) seems to be more reactive than diethylamino Ib. Significant differences between the two carbonium ions were observed in reactions with aniline and with sodium cyanide. Carbonium ion Ia reacted with aniline to give 2-phenylimino-1,3-dithiolane (IVa) in a good yield, while Ib did not afford (IVa) but a small amount of *N*,*N'*-diphenylthiourea. With cyanide ion, Ia afforded 2-cyano-2-dimethylamino-1,3-dithiolane (IXa), while Ib did not produce diethylamino derivative (IXb) but a complex mixture.

Examination of stuructures of products reveals the following facts: (i) as expected, 2-dialkylamino-1,3-dithiolanylium ions (I) are ambident electrophiles with two reactive sites, *i.e.*, the electron-deficient centered carbon atom (a) and the ring-methylene neutral carbon atoms (b); (ii) in contrast to behaviors of ambident nucleophiles toward electrophilic reagents,[10] reactions between these ambident electrophiles and the nucleophilic reagents proceed in a more straightforward manner; (iii) the nature of nucleophile (Nu^-) greatly affects the reaction course, which may be classified into three modes (Chart 2).

Mode A involves initial attack of the nucleophile at the site (a) with the retention of the ring structure to yield adduct X, which, in turn, undergoes various subsequent reactions. Nucleophiles which react *via* mode A are oxygen nucleophiles, aryl amines and cyanide ion. The proton transfer from

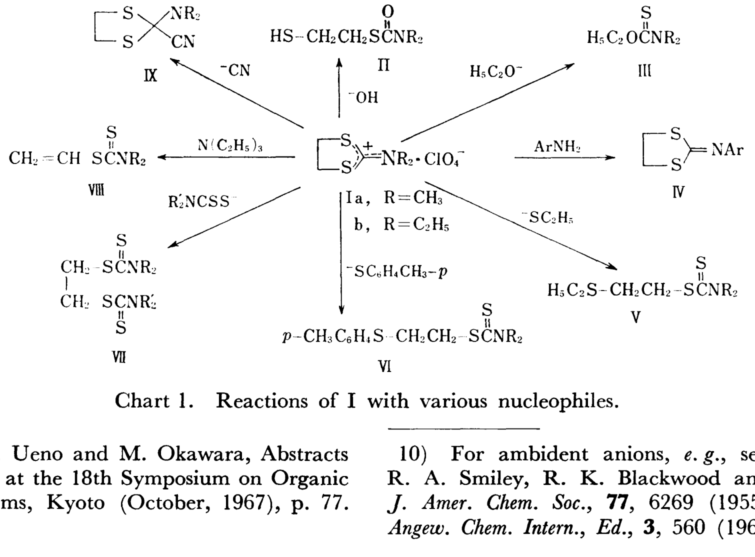


Chart 1. Reactions of I with various nucleophiles.

---

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

[10] For ambident anions, *e.g.*, see N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *J. Amer. Chem. Soc.*, **77**, 6269 (1955); R. Gompper, *Angew. Chem. Intern., Ed.*, **3**, 560 (1964).

TABLE 1. REACTIONS OF I WITH NUCLEOPHILES

Starting materials		Conditions			Product [a]	Yield [b] (%)
Perchlorate	Nuleophile (mol ratio)	Solvent	Temp. °C	Time hr		
Ia	H_2O/NEt_3 (2.0)	DMF	80	3	IIa, $R=CH_3$	30
Ib	H_2O/NEt_3 (2.0)	DMF	80	3	IIb, $R=C_2H_5$	28
Ia	$NaOC_2H_5$ (3.0)	Dioxane	reflux	2	IIIa, $R=CH_3$	52
Ib	$NaOC_2H_5$ (3.0)	Dioxane	reflux	6	IIIb, $R=C_2H_5$	82
Ia	$C_6H_5NH_2$ (2.0)	DMSO	80	4	IVa, $Ar=C_6H_5$	70
Ia	p-$CH_3C_6H_5NH_2$ (2.0)	DMSO	80	4	IVb, $Ar=p$-$CH_3C_6H_4$	77
Ib	$C_6H_5NH_2$ (2.0)	DMSO	80	4	*N,N′*-diphenylthiourea [c]	8
Ia	$NaSC_2H_5$ (1.0)	DMF	60	4	Va, $R=CH_3$	36
Ib	$NaSC_2H_5$ (1.0)	DMF	60	4	Vb, $R=C_2H_5$	(38) [d]
Ia	$NaSC_6H_4CH_3$-p (1.0)	DMF	60	4	VIa, $R=CH_3$	77
Ib	$NaSC_6H_4CH_3$-p (1.0)	DMF	60	4	VIab, $R=C_2H_5$	59
Ia	$NaSCSN(CH_3)_2$ (1.0)	DMF	60	4	VIIa, $R=CH_3, R'=CH_3$	95
Ia	$NaSCSN(C_2H_5)_2$ (1.0)	DMF	60	4	VIIb, $R=CH_3, R'=C_2H_5$	90
Ib	$NaSCSN(CH_3)_2$ (1.0)	DMF	60	4	VIIb	92
Ib	$NaSCSN(C_2H_5)_2$ (1.0)	DMF	60	4	VIIc, $R=C_2H_5, R'=C_2H_5$	85
Ia	$N(C_2H_5)_3$ (2.0)	DMSO/Diox.	75	2	VIIIa, $R=CH_3$	65
Ib	$N(C_2H_5)_3$(2.0)	DMSO/Diox.	70	3	VIIIb, $R=C_2H_5$	63
Ia	NaCN(3.0)	DMF	60	4	IXa, $R=CH_3$	64
Ib	NaCN (3.0)	DMF	60	4	e)	

a) Numbers refer to compounds in Chart 1.
b) Based upon Ia or Ib. No attempt was made to maximize conditions.
c) In contrast to Ia, Ib did not produce IVa at all.
d) Both UV and IR spectra suggested that this fraction was contaiminated with *S*-vinyl dithiocarbamate (VIIIb).
e) In contrast to Ia, Ib did not afford IXb ($R=C_2H_5$), but a complex mixture.

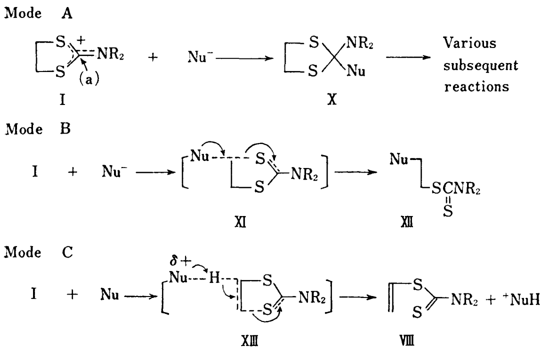


Chart 2. Reaction modes.

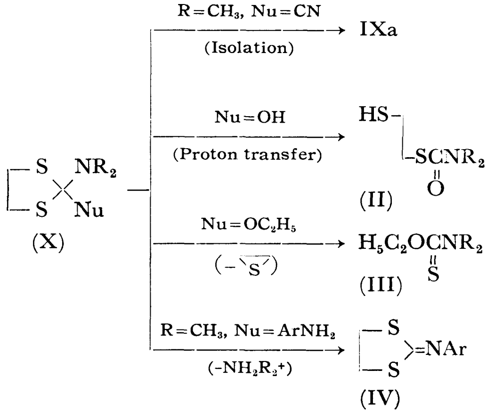


Chart 3. Subsequent reaction of X.

X (Nu=OH) results in the formation of VI, while loss of episulfide from X (Nu=OEt) can account for the formation of thioncarbamate (III).[11] Formation of IV from Ia and aniline can be interpreted by deamination of adduct X ($Nu=ArNH_2$) (Chart 3).

Mode B involves initial attack of the nucleophile at the site (b) to give *β*-substituted ethyl dithiocarbamate (XI). Nucleophiles which react *via* mode B are all sulfur nucleophiles examined. Attack of the nucleophiles to (b) might proceed through the S_N2-type mechanism, *i.e.*, *via* transition state XI,

---

[11] For elimination of episulfide from sulfur-containing heterocyclics, see R. Feinaer, *Angew. Chem. Intern., Ed.*, **5**, 894 (1966). We have also observed that ethylene oxide cyclo-adds to the thiocarbonyl group to give the corresponding carbonyl compound involving loss of episulfide from the cyclo-adduct: Y. Ueno, T. Nakai and M. Okawara, This Bulletin, **43**, 168 (1970).

which has been kinetically verified with the reaction of Ia with sodium *N,N*-dimethyldithiocarbamate.[2] This fact is also supported by the observation that the yield of XII under similar conditions (see Table 1) increases with an increase in nucleophilicity of the attacking reagent, being in the order: $C_2H_5S^- < p\text{-}CH_3C_6H_4S^- < R'_2NCSS^-$[12] for both carbonium ions.

Finally, there are two possible mechanisms for the formation of *S*-vinyl dithiocarbamates (VIII) from I and triethylamine. The first mechanism involves the Hofmann elimination of tetraalkylammonium salt XII ($Nu = NEt_3$) formed *via* mode B. The other consists of mode C which involves initial abstraction of the proton of the ring-methylene followed by the ring scission through the well-known concerted mechanism accepted for the general E2 reaction. It seems reasonable to assume that mode C is operative since triethylamine is basic and so combines more preferentially with the proton that the neutral carbon atom bearing the proton.

It may be roughly summarized that if the nucelophile is basic, *e.g.*, OH^- or RO^-, mode A is favored, but if it has large substituents, *e.g.*, NEt_3, the initial proton abstraction (mode C) is predominant. On the other hand, if the nucleophile is polarizable, *e.g.*, RS^- or R_2NCSS^-, mode B is favored. According to the concept of soft and hard acids and bases,[13] it can also be said that hard bases react *via* mode A while soft bases react *via* mode B, and that, with respect to the carbonium ion, the reactive site (a) is hard and (b) is soft.

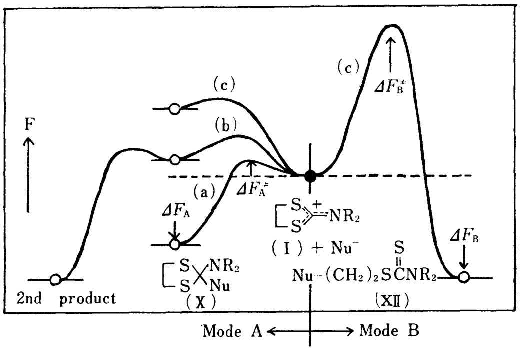


Fig. 1. Schematic energy profiles for mode A and B: curve (a), $Nu^- =$ *e.g.*, ^-CN; (b), $Nu^- =$ *e.g.*, ^-OH; (c), $Nu^- =$ *e.g.*, $^-SCSNR_2$. Strictly speaking, the energy content of the initial system, I^+ and Nu^-, depends upon the nature of Nu^-.

We might conclude that the nature of the nucleophile largely changes the reaction course, though the factors deciding the reaction course remain unknown. To clarify this point, the schematic energy profile of the overall reaction was considered tentatively (Fig. 1).[14]

Since the primary process of mode A corresponds to a simple association between the cation and the anion, the free activation energy ($\Delta F_A^{\ddagger}$) is always less than that for mode B ($\Delta F_B^{\ddagger}$). It may be assumed that the position of the equilibrium between cation I and adduct X in mode A should depend upon the difference in ΔF_A between I and X, *i.e.*, upon their relative position in the energy diagram, except for steric factors. On the other hand, since the transformation of I into XII in mode B results in release of the mesomeric energy of XII as well as the energy of charge neutralization, product XII must be a thermodynamically stable product, *i.e.*, $\Delta F_B > \Delta F_A$. Both ΔF_B and $\Delta F_B^{\ddagger}$ may be assumed to be very large since mode B is irreversible. In short, it can approximately be said that the primary reaction of mode A is kinetically controlled, while mode B is thermodynamically controlled. These discussions substantially lead to the hypothesis that the major factor deciding the reaction course is the relative position of the kinetically controlled product (X) in the energy diagram, *i.e.*, the magnitude of ΔF_A (Fig. 1). Since the small free activation energy ($\Delta F_A^{\ddagger}$) changes only slightly with the nature of nucleophile, kinetic adduct (X) can be isolated only when a strong nucleophile such as CN^- was used (Table 1). In the case where the primary adduct is not so stable, if the adduct may be readily converted into the more stable second product by various irreversible reactions (Chart 3), the reaction will be also directed to mode A, while if adduct (X) cannot undergo such second irreversible reactions, the reaction will be directed to mode B, as has been observed in the reactions with sulfur nucleophiles. Naturally $\Delta F_B^{\ddagger}$ depends upon the nucleophilicity of the attacking reagent; this accounts for the difference in yield of product XII with a series of sulfur nucleophiles.

This may qualitatively explain behaviors of all nucleophiles except triethylamine toward the ambident electrophiles (Table 1). The fact that triethylamine reacts with I *via* mode C, not *via* mode A, might be expained by the steric factor, *i.e.*, both by an increase of $\Delta F_A^{\ddagger}$ and a decrease of ΔF_A. In all cases, from these qualitative results it is difficult to determine whether the major factor deciding the reaction course is the stability of kinetic adduct (X) or the steric factor. Further quantitative data based upon kinetic studies are required to ascertain this point.

---

12) Dithiocarbamate anions are ranked with the strongest nucleophiles in aqueous solutions: R. E. Davis, "Survey of Progess in Chemistry," ed. by A. Scott, Vol. 2, Academic Press Inc., New York, N. Y. (1964), p. 189; R. E. Davis, H. Nakshbendi and A. Ohno, *J. Org. Chem.*, **31**, 2702 (1966).

13) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

14) For analogous considerations, see Ref. 4; S. Winstein and E. M. Kosower, *J. Amer. Chem. Soc.*, **81**, 4399 (1959); J. Miller, *ibid.*, **85**, 1628 (1963).

Experimental

General. Melting and boiling points are uncorrected. The infrared spectra were recorded with a Hitachi EPI-S2 spectrometer. Ultraviolet spectra were recorded with a Hitachi EPS-2 spectrometer. Nuclear magnetic resonance spectra were determined with either a Varian Associates A-60 or a Japan Electron Optics C-60 spectrometers. Chemical shifts are given in a parts per million (ppm) from tetramethylsilane as an internal standard. All nucleophilic reagents employed were either commercially available materials or prepared by a standard method.

2-Dimethylamino-1,3-dithiolanylium Perchlorate (Ia). To a solution of 39.0 g (0.40 mol) of 1,2-dichloroethane in 80 m*l* of ethanol, was added a solution of sodium *N*,*N*-dimethyldithiocarbamate (72.0 g, 0.40 mol) in 120 m*l* of ethanol. The mixture was stirred at 55°C for 3 hr. Sodium chloride formed was filtered off and the filtrate was concentrated under reduced pressure. The mixture was poured into 300 m*l* of cold water to give 4.2 g of white precipitates, ethylene bis(*N*,*N*-dimethyldithiocarbamate): mp 187—189°C. To the resulting aqueous solution was added sodium perchlorate (45 g) to give 62.0 g (62%) of white precipitates (Ia): mp 179—180°C (acetone) (lit,[2] 179—180°C); UV: λ_{max} (H_2O) 249 mμ ($\varepsilon=1.31\times10^4$).

2-Diethylamino-1,3-dithiolanylium Perchlorate (Ib). In a similar fashion the reaction of sodium *N*,*N*-diethyldithiocarbamate with 1,2-dichloroethane gave perchlorate Ib in 44% yield; mp 89—90°C (water); UV: λ_{max} (H_2O) 255 mμ.

Found: C, 30.62; H, 5.15; N, 5.01%. Calcd for $C_7H_{14}ClNO_4S_2$: C, 30.38; H, 5.12; N, 5.08%.

Hydrolyses of Salt I. Salt Ia (6.2 g, 0.025 mol) was added to a solution of 1.0 g (0.01 mol) of triethylamine and 1.0 g (0.05 mol) of water in 15 m*l* of dimethylformamide (DMF). The reaction mixture was stirred at 100°C for 3 hr, then poured into cold water. The mixture was extracted several times with ether. The ether layer was dried over sodium sulfate and the solvent evaporated *in vacuo*. Distillation of the residue gave 1.2 g of β-mercaptoethyl *N*,*N*-dimethylthiolcarbamate (IIa): bp 85—87°C/2 mmHg; n_D(25°C) 1.6038; IR (neat): 1650 (C=O) and 1490 cm^{-1} (N–CO). The physical properties and spectral data of this distillate were in agreement with those of the authentic sample.[2]

Hydrolysis of salt Ib carried out as in the case of Ia yielded 2.0 g of thiolcarbamate IIb: bp 116—118°C/2 mmHg; n_D(20°C) 1.5800; IR (neat): 1650 and 1495 cm^{-1}.

Both these products discolored an aqueous solution of iodine and gave mercury mercaptide on treatment with mercuric chloride indicating the presence of a mercapto group.

Reactions of Salt I with Sodium Ethoxide. Salt Ia (12.5 g, 0.05 mol) was added to a suspension of 10.2 g (0.15 mol) of sodium ethoxide in 70 m*l* of dioxane. The mixture was stirred at 100°C for 2 hr in a nitrogen atmosphere, then poured into water. The ether layer was dried over sodium sulfate and the solvent was evaporated. Distillation of the residue gave 3.5 g (52%) of ethyl *N*,*N*-dimethylthioncarbamate (IIIa): bp 81—82°C/10 mmHg; n_D(25°C) 1.5082; UV (EtOH): 250 and 285 mμ (shoulder) (lit, bp 82.6°C/10 mmHg;[15] n_D(20°C) 1.5075;[16] UV: 250 and 285 mμ (shoulder)[17]).

The reaction of Ib with sodium ethoxide carried out as in the case of Ia gave ethyl *N*,*N*-diethylthioncarbamate (IIIb) in 82% yield; bp 99—101°C/13 mmHg; n_D(23°C) 1.4968 (lit, bp 114°C/20 mmHg;[18] n_D(15°C) 1.5021[19]); UV (EtOH): 250.5 and 290 mμ (shoulder). The infrared spectrum of IIIb was in agreement with that of the authentic sample.[20]

Reactions of Salt I with Anilines. Salt Ia (6.2 g, 0.025 mol) was added to a solution of 5.0 g (0.05 mol) in aniline in 40 m*l* of dimethylsuldefoxide (DMSO). The reaction mixture was stirred at 80°C for 3.5 hr, then poured into water. The ether layer was dried over sodium sulfate and the solvent and unreacted aniline were removed *in vacuo*. Recrystallization of the residue from ethanol gave 3.6 g (73%) of 2-phenylimino-1,3-dithiolane (IVa): mp 47—48°C; IR (KBr): 1570 cm^{-1} (C=N); NMR (CCl_4): δ 3.32 (s, CH_2S) and 6.55—7.10 ppm (m, aromatic protons).

Found: C, 55.48; H, 4.89; N, 7.00%. Calcd for $C_9H_9NS_2$: C, 55.38; H, 4.65; N, 7.18%.

Imino-dithiolane IVa reacted with hydroxylamine in ethanol giving 2-hydroxyimino-1,3-dithiolane: mp 122—124°C (lit,[21] 124—127°C); IR (KBr): 3100 (OH) and 1590 cm^{-1} (C=N).

The reaction of Ia with *p*-toluidine was carried out as in the case of aniline. Salt Ia (6.2 g, 0.025 mol) and *p*-toluidine (5.0 g, 0.05 mol) gave 4.8 g (77%) of a yellowish oil (IVb); IR (neat): 1580 cm^{-1} (C=N). The oil was treated with a 6N alcoholic solution of hydrogen chloride to give white precipitates of the hydrochloride: mp 209—211°C (lit,[22] 190—192°C).

Found: C, 48.52; H, 4.99; N, 5.62%. Calcd for $C_{11}H_{11}ClNS_2$: C, 48.89; H, 4.92; N, 5.73%.

By the same procedure the reaction of Ib (7.0 g, 0.025 mol) with aniline (5.0 g, 0.05 mol) gave 0.5 g of *N*,*N'*-diphenylthiourea as only ether-soluble product.

Reactions of Salt I with Sodium Ethylmercaptide. Salt Ia (12.5 g, 0.05 mol) was added to a solution of 4.2 g (0.05 mol) of sodium ethylmercaptide in 40 m*l* of DMF. The reaction mixture was stirred at 70°C for 5 hr, then poured into cold water. The carbon tetrachloride layer was dried over sodium sulfate and the solvent evaporated *in vacuo*. Distillation of the residue gave 3.6 g (36%) of a pale oil, β-(ethylthio)ethyl *N*,*N*-dimethyldithiocarbamate (Va): bp 67—68°C/0.14 mmHg; n_D(22°C) 1.5819; IR (neat): 1500 cm^{-1} (N–CS);[23] UV (EtOH): 250 and 278 mμ.[24]

---

[15] O. Billeter, *Ber.*, **43**, 1853 (1910).

[16] B. Holmberg, *Svensk. Kim. Tids.*, **41**, 249 (1929).

[17] M. J. Janssen, *Rec. Trav. Chim.*, **79**, 454 (1960).

[18] A. Hantzsch, *Ber.*, **64**, 661 (1931).

[19] M. Delepine, *Ann. Chim. Phys.*, (8)**25**, 529 (1912).

[20] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. IV, Chemical Publ. Inc., New York, N. Y. (1962), p. 202.

[21] R. W. Addor, U. S. 3193561 (1965); *Chem. Abstr.*, **63**, 11577 (1965).

[22] A. Miolati, *Ann. Chem.*, **262**, 61 (1891).

[23] The thioureisd band of dithiocarbamates: **H. M.** Randall, R. G. Fowler, N. Fuson and J. Dangl, "Infrared Determination of Organic Structure," Van Nostrand, New York, N. Y. (1949).

Found: C, 39.82; H, 7.53; N, 6.99%. Calcd for $C_7H_{15}NS_3$: C, 40.19; H, 7.53; N, 6.99%.

By the same procedure the reaction of salt Ib (14.0 g, 0.05 mol) with sodium ethylmercaptide (4.2 g, 0.05 mol) gave 4.5 g of a pale-yellowish oil: bp 84—86°C/0.4 mmHg; UV (EtOH): λ_{max} 250 and 280 mμ.[24] The IR spectrum of the distillate showed an absorption band at 1600 cm^{-1} (C=C) as well as bands presumably due to β-(ethylthio)ethyl *N*,*N*-diethyldithiocarbamate (Vb). In comparison with the IR spectrum of *S*-vinyl *N*,*N*-diethyldithiocarbamate (VIIIb), the spectrum indicates that the distillate was contaimnated with a small amount of VIIIb.

Reactions of Salt I with Sodium *p*-Tolylmercaptide. Salt Ia (6.3 g, 0.025 mol) was added to a solution of 4.0 g (0.027 mol) of sodium *p*-tolylmercaptide in 40 m*l* of DMF. The reaction mixture was stirred at 70°C for 5 hr, then poured into cold water. The carbon tetrachloride layer was dried over sodium sulfate and the solvent evaporated. Recrystallization of the residue from ethanol gave 5.7 g (77%) of β-(*p*-tolylthio)ethyl *N*,*N*-dimethyldithiocarbamate (VIa): mp 48—49°C; IR (KBr): 1495 cm^{-1} (N-CS);[23] UV (EtOH): λ_{max} 257 and 278 (shoulder);[24] NMR (CCl_4): δ 2.30 (s, $C\underline{H}_3C_6H_4$), 3.42 (s, CH_3-N), 3.10—3.80 (m, S-$C\underline{H}_2$-$C\underline{H}_2$-S-CS) and 6.80—7.40 ppm (m, aromatic protons).

Found: C, 52.86; H, 6.25; N, 4.95%. Calcd for $C_{12}H_{17}NS_3$: C, 53.13; H, 6.32; N, 5.16%.

In a similar fashion the reaction of salt Ib (10.4 g, 0.042 mol) with sodium *p*-tolylmercaptide (5.5 g, 0.037 mol) was carried out. Distillation of the oily residue gave 6.5 g (59%) of β-(*p*-tolyl)ethyl *N*,*N*-diethyldithiocarbamate (VIb): bp 165—170°C/0.6 mmHg; n_D(20°C) 1.6426; UV (EtOH): λ_{max} 257 and 278 mμ (shoulder).[24]

Found: N, 4.82%. Calcd for $C_{14}H_{21}NS_3$: N, 4.68%.

Reactions of Salt I with Sodium Dithiocarbamates. Salt Ia (2.5 g, 0.01 mol) was added to a solution of 1.8 g (0.01 mol) of sodium *N*,*N*-dimethyldithiocarbamate in 25 m*l* of DMF. The mixture was stirred at 60°C for 4 hr, then poured into cold water giving 2.4 g (96%) of white precipitates, ethylene bis(*N*,*N*-dimethyldithiocarbamate) (VIIa): mp 188—189°C (DMF) (lit,[25] 188—190°C).

By the same procedure salt Ib (2.8 g, 0.01 mol) and the same dithiocarbamate salt (1.8 g, 0.01 mol) gave 2.5 g (92%) of ethylene bis(*N*,*N*-dimethyl-*N'*,*N'*-diethyldithiocarbamate) (VIIb): mp 102—103°C (ethanol); UV (EtOH): 253 and 279 mμ.[24]

Found: C, 40.42; H, 6.92; N, 9.11%. Calcd for $C_{10}H_{20}N_2S_4$: C, 40.54; H, 6.80; N, 9.46%.

Similarly the reaction of salt Ia with sodium *N*,*N*-diethyldithiocarbamate yielded VIIb in 90% yield. On the other hand, the reaction of salt Ib with the same dithiocarbamate salt gave ethylene bis(*N*,*N*-diethyldithiocarbamate) (VIIc): mp 93—94°C (ethanol) (lit,[26] 94—95°C); UV (EtOH): λ_{max} 254 and 280 mμ.[24]

Reactions of Salt I with Triethylamine. Salt Ia (12.5 g, 0.05 mol) was added to a solution of 6.0 g (0.06 mol) of triethylamine in a mixture of DMSO (30 m*l*) and dioxane (20 m*l*). The reaction mixture was stirred at 60°C for 5 hr, then poured into water. The ether layer was dried and the solvent evaporated. Distillation of the residue gave 2.0 g (65%) of a pale-yellowish oil, *S*-vinyl *N*,*N*-dimethyldithiocarbamate (VIIIa): bp 87—90°C/2 mmHg; n_D(25°C) 1.5907 (lit,[27] bp 82—83°C/1 mmHg; n_D(20°C) 1.6025); IR (neat): 1590 cm^{-1} (C=C); UV (EtOH): 253 and 280 mμ (shoulder).

By the same procedure the reaction of salt Ib with triethylamine gave *S*-vinyl *N*,*N*-diethyldithiocarbamate (VIIIb) in 63% yield: bp 80—84°C/0.1 mmHg (lit,[28] 92—94°C/2 mmHg); n_D(25°C) 1.5942; IR (neat): 1600 cm^{-1} (C=C); UV (EtOH): 258 and 280 mμ (shoulder).

Found: C, 48.23; H, 7.86; N, 7.96%. Calcd for $C_7H_{13}NS_2$: C, 47.99; H, 7.48; N, 8.00%.

The IR spectra of these products were identical with those of the authentic samples.[27]

Reactions of Salt I with Sodium Cyanide. Salt Ia (12.5 g, 0.05 mol) was added to a solution of 7.5 g (0.15 mol) of sodium cyanide in 50 m*l* of DMF. The reaction mixture was stirred at 60°C for 4 hr, then poured into water. The ether layer was dried and the solvent evaporated. Distillation of the residue gave 5.2 g (64%) of a yellowish oil, 2-cyano-2-dimethylamino-1,3-dithiolane (IXa): bp 114—116°C/3 mmHg; n_D(27°C) 1.5633; IR (neat): 2250 cm^{-1} (C≡N); NMR (CCl_4): δ 2.47 (s, CH_3-N) and 3.37 ppm (s, CH_2-S).

Found: N, 15.69%. Calcd for $C_6H_{10}N_2S_2$: N, 16.09%.

By the same procedure the reaction of salt Ib (14.0 g, 0.05 mol) and sodium cyanide (7.5 g, 0.15 mol) gave 4.8 g of a yellowish oil: bp 83—85°C/0.2 mmHg. This distillate was proved to be not 2-cyano-2-diethylamino-1,3-dithiolane, but a complex mixture by the IR spectrum (neat) exhibiting several absorption bands due to the -S-CS-N< structure as well as C=C and C≡N groups.

---

[24] The characteristic bands due to the -S-CS-N< structure. The higher wavelength band is associated with transition to the imminium state (*N*-conjugation) while the lower wavelength feature arises from transition to the sulfonium state (*S*-conjugation): M. J. Janssen, *Rec. Trav. Chim.*, **79**, 454, 464 (1960).

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

[26] K. Pilgram, D. Phillips and F. Korte, *J. Org. Chem.*, **29**, 1848 (1964).

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

[28] J. C. Sauer, *J. Org. Chem.*, **24**, 1592 (1959).