Reaction of 1,3-Dithiolium Cation with Xanthate and Dithiocarbamate Anions[1]

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The reactivity of 4-aryl-1,3-dithiolium cation (1) toward sulfur nucleophiles was investigated. The initial adduct obtained from reaction of 1 with ethyl xanthate (2) was found to react further with 2 in an appropriate solvent. Dithiocarbamate anion (3) reacted with 1 to give the 1,3-dithiol-2-yl ester derivative (8), which is unstable in solution even at room temperature and undergoes thermal decomposition into the 2-disubstituted amino-1,3-dithiole derivative (10) with loss of carbon disulfide. Except for the acyl ester (mixed carboxylic dithiocarbamic anhydride), ester 8 is the first example for which the decomposition mechanism has been elucidated. The facile decomposition is due to the existence of concurrent product-catalyzed decomposition. The presence of an electron-donating group at the para position of the 4-phenyl of 8 enhances decomposition, which is accelerated ninefold in EtOH compared with the rate in CH_3CN. Activation parameters for the first-order decomposition of 8m in EtOH and MeCN are $\Delta H^{\ddagger}$ = 16.5 and 22.0 kcal/mol and $\Delta S^{\ddagger}$ = −21.5 and −6.11 eu, respectively. The decomposition mechanism is discussed in the light of these data.

1,3-Dithiolium cation (1) is a 6-π-electronic system in a positively charged five-membered ring and is highly stabilized by delocalization of the π electrons. The positive charge is also delocalized over all of the ring atoms by valence expansion of the sulfur atoms. A high positive charge density on C-2 leads to high reactivity toward nucleophilic reagents, and a C-2 adduct (2-substituted 1,3-dithiole) can be obtained with ease.[2] Thus, in view of their nonbenzenoid aromaticity and reactivity, 1,3-dithiolium cations form an interesting class of versatile compounds.

We have previously studied the behavior of 1 toward a variety of nucleophiles,[3] and have investigated its heteroaromaticity.[4] Continuing this work, we studied the nucleophilic reaction of 1 with xanthate (2) and dithiocarbamate (3) anions. The initially produced C-2 adducts of 2 reacted further with nucleophiles, 2 or benzylmercaptide anion, in an appropriate solvent, and the C-2 adducts of 3 decomposed easily in solvents with loss of carbon disulfide.

Results

Reaction of 4-Phenyl-1,3-dithiolium Perchlorate (1a) with Potassium Ethylxanthate (2). Reaction of 1a with 2 mol of 2 (excess of nucleophile) in acetone afforded sulfide 4a, and not the expected C-2 adduct. NMR of 4a showed C-2 and C-5 protons of the 1,3-dithiole ring in addition to phenyl protons. The mass spectrum of 4a showed dithiolium cation (4-phenyl, *m/e* 179) as the base peak, a common decomposition pattern for C-2 adduct. The structure of 4a was thus ascertained by spectral and analytical data. Treatment of 4a with perchloric acid yielded 4-phenyl-1,3-dithiolium cation (1a) with evolution of hydrogen sulfide. Compound 4a was also identified as the product of the reaction of 1a with sodium sulfide in water (Figure 1).

When this reaction was carried out in acetonitrile with an equimolar amount of 2, C-2 adduct (5a) was obtained as an oil; its structure was ascertained by NMR and analytical data. To confirm the formation of 4 by further reaction of 5 with 2, 5 was treated with 2 in acetone, giving 4a in high yield. Furthermore, reaction of 5a with sodium benzylmercaptide afforded 4a in addition to a transesterified product (6). Also, reaction of 5a with alkoxide ion in the corresponding alcohol gave 2-alkoxy-4-phenyl-1,3-dithiole (7).

Reaction of 1 with Sodium N,N-Disubstituted Dithiocarbamate (3). Nucleophilic reaction of 3 toward 1 gave C-2 adduct (8) in moderate yield. The structure of 8 was assigned with spectral and analytical data (Table I).

When 2-dialkylamino-4-aryl-1,3-dithiolium perchlorate (9) was treated with 3, a yellow solid not soluble in many solvents (Me_2SO, CH_3CN, EtOH, $CHCl_3$) was isolated. A saturated solution of 9 in ethanol and acetone showed a UV maximum at 380 and 386 nm, respectively, and the analytical data suggested it to be a 1:1 adduct of a cation and anion species (Table I). These data indicate that 9a–d are anion-exchange products. The visible absorption is due to a charge-transfer band, such as has been reported for pyridinium dithiocarbamate.[5]

In contrast to the reactivity of 5 toward nucleophiles, 8 and 9a–d are stable in the solid state, though the former is less stable. However, a displacement reaction of 8 takes place with secondary amine or dithiocarbamate anion. And, in solution, 8 undergoes unusually rapid decomposition into 2-disubstituted amino-4-aryl-1,3-dithiole (10) with essentially quantitative evolution of carbon disulfide. The appropriate 10 was isolated in good yield by thermolysis of 8 in solvent (see Experimental Section). Decomposed product (10) was also obtained by the reaction of 1 with the corresponding amine,[3] or reduction of 2-disubstituted amino-4-aryl-1,3-dithiolium cation with $NaBH_4$ (Figure 2).[20]

Dithiocarbamate esters are in general unstable in solution, decomposing into amine derivatives and CS_2 photochemically[6] or thermally.[7] To elucidate the mechanism of decomposition of 8 in solution, we studied the kinetics spectroscopically. The rate constant for thermolysis of 8 was estimated by the decrease in the absorption coefficient at 257 nm, where the absorption of carbon disulfide did not overlap. The first-order plot, which was obtained from UV data, deviates upward from linearity with the progress of decomposition. The plot, in which the product-catalyzed term was taken into consideration,[8]

$$dx/dt/(a - x) \text{ vs. } x^2$$

has a good linear relationship as shown in Figure 3. This indicates that the second-order catalytic term with respect to 10 takes place. The intercept of the plot in Figure 3 is the first-order decomposition rate constant, k_0, and the slope is the catalyzed rate constant, k_2. With the progress of decomposition (>75%), the plot of Figure 3 deviates upward further from linearity. Table II summarizes k_0 and k_2 which were evaluated from Figure 3.

The k_0 values in EtOH, which has strong ionizing power, are about nine times larger than those in MeCN. The substituent R_1, which has an electron-donating character, accelerates the decomposition. On the other hand, the substituent effect of the aromatic ring attached to nitrogen is the reverse of that of R_1. The existence of the k_2 term in addition to the k_0 term is the main reason for the facile decomposition

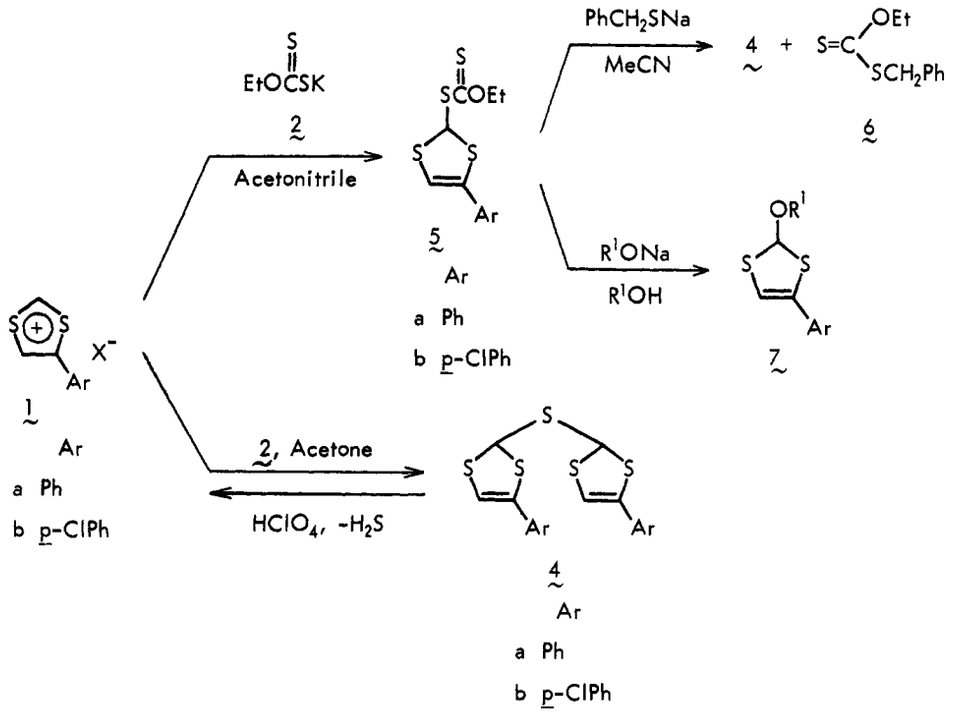


Figure 1. Reaction of 4-phenyl-1,3-dithiolium cation (1) with xanthate anion (2).

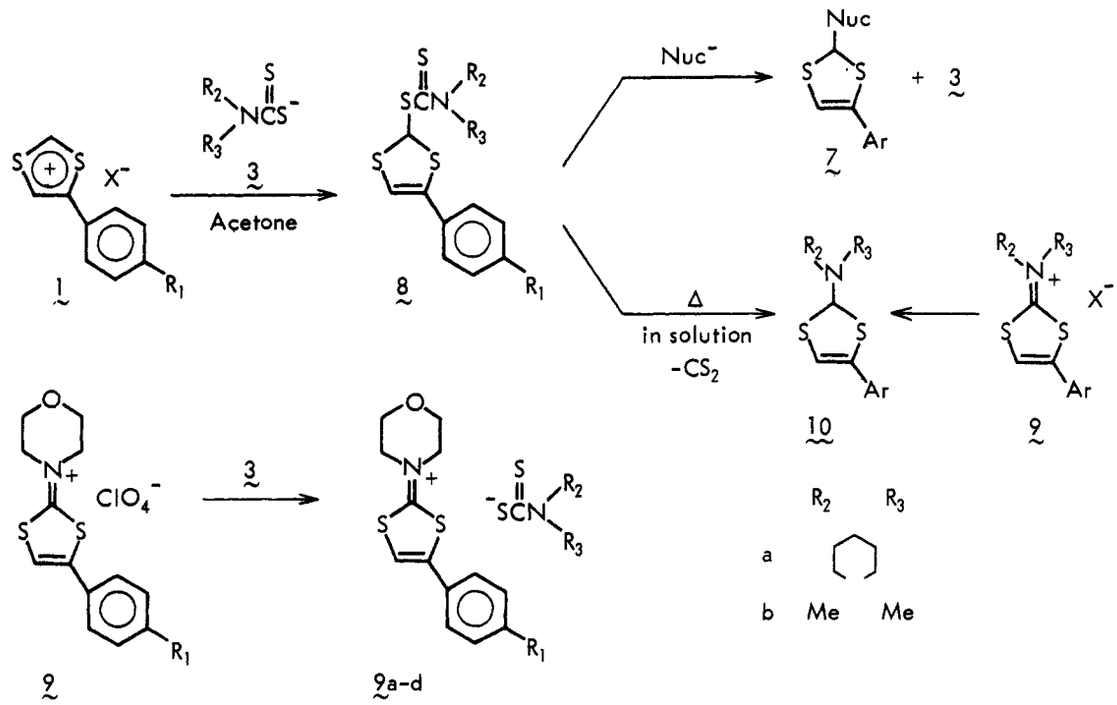


Figure 2. Reaction of 4-phenyl-1,3-dithiolium cation (1) with dithiocarbamate anion (3).

of 8. The activation parameters obtained from the plot of log k_0 against $1/T$ are shown in Table III. The large difference in k_0 and $\Delta S^{\ddagger}$ between the solvents EtOH and MeCN indicates that the decomposition mechanisms are not the same.

From the Hammett plot toward σ^+ from the data of runs 11–14 in Table II, we obtained $\rho = -0.57$ and -0.38 for k_0 and k_2, respectively. The data of run 15 deviate downward from this slope. Decomposition did not occur in the presence of base (OH^-); substitution at C-2 of the dithiole ring took place instead.

Discussion

Although the positive charge of 1,3-dithiolium cation can be delocalized over all ring atoms, no report on the nucleophilic attack taking place at other than the C-2 carbon has appeared.[9] Initial adducts obtained from nucleophilic reaction of 1 with nucleophile are generally stable. However, 5 has several reactive sites for futher nucleophilic attack, which took place at one of its reaction centers in a suitable solvent.[10] The reaction route for the formation of 4 is shown in Figure 4.

Refluxing 5 in acetone does not yield 4, indicating that another reagent is necessary and the reaction is not a Chugaev-type pyrolysis.[11] As shown in Figure 4, in the reaction between 1 and 2 in acetone, 2 attacks as a nucleophile at the thion carbon of adduct 5 to release R^0S^- (R^0 = 4-aryl-1,3-dithiol-2-yl) anion (if benzylmercaptide anion was used instead of 2, transesterified xanthate ester was obtained). The R^0S^- thus formed further attacks the C-2 carbon of the five-membered

Table I. *S*-(4-Aryl-1,3-dithiol-2-yl) N,N-Disubstituted Dithiocarbamates (8)[a] and 4-Aryl-2-morpholino-1,3-dithiolium N,N-Disubstituted Dithiocarbamates (9)[a]

Compd 8	R_2	R_3	R_1	Mp, °C	Yield, %
a	Me	Me	H	80–81	89
b	Me	Me	Br	124–125	85
c	Me	Me	Cl	106–108	85
d	Me	Me	OCH_3	112–114	82
e	Me	Me	CH_3	119–122	85
f	Me	Me	OH	106–108	69
g	Et	Et	H	81–83	87
h	*n*-Pr	*n*-Pr	H	82–83	86
i	*i*-Pr	*i*-Pr	H	94–96	85
j	*n*-Bu	*n*-Bu	H	61–62	63
k	$PhCH_2$	$PhCH_2$	H	87–88	53
l	$-(CH_2)_5-$		H	120–122	82
m	$CH_2CH_2OCH_2CH_2$		H	121–122	51
n	$CH_2CH_2OCH_2CH_2$		OMe	114–115	73[b]
o	$CH_2CH_2OCH_2CH_2$		Br	116–117	74
p	Me	Ph	H	129–131	30
q	Me	Ph	OMe	146–147	47
r	Me	Ph	Br	121–124	38
s	Me	*p*-MeOPh	H	127–128	28
t	Me	*p*-MeOPh	Cl	138–140	41

9				Mp, °C dec	
a	H	Ph	H	130–131	72
b	$-CH_2CH_2OCH_2CH_2-$		H	152–153	81
c	$-CH_2CH_2OCH_2CH_2-$		OMe	160–165	86
d	$-CH_2CH_2OCH_2CH_2-$		Cl	158–160	68

[a] Satisfactory analytical values (±0.3% for C, H, N, and S) were submitted for all compounds except **8n**. [b] Exact analytical data were not obtained for **8n** owing to its thermal instability.

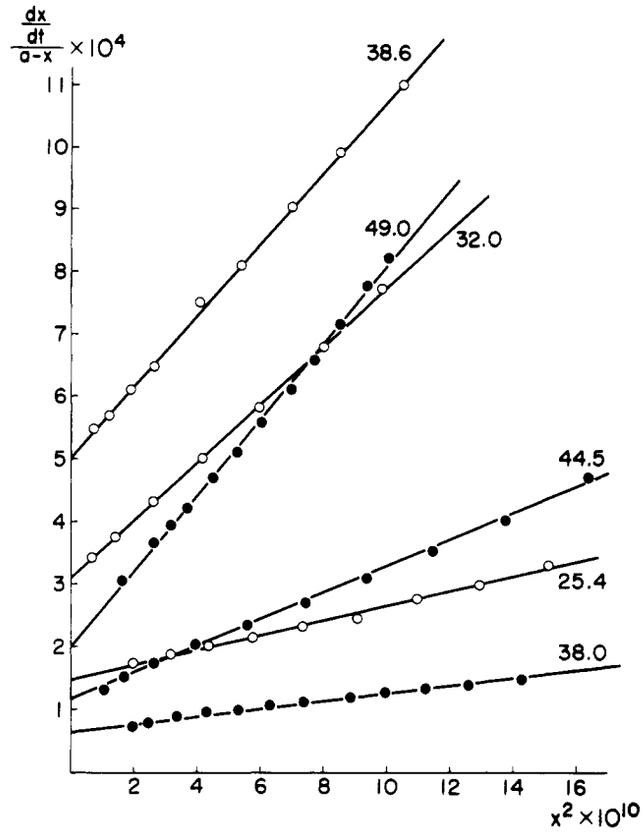
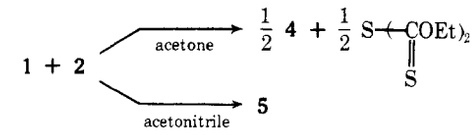


Figure 3. Plot of $dx/dt/(a - x)$ vs. x^2: ●, MeCN; ○, EtOH. Temperatures are shown in the figure.



ring of **5**, and substitution reaction leads to the formation of **4**. At this point, xanthate anion is reproduced. Thus for the reaction of **5** with **2** an equimolar amount of **2** is not necessary, a catalytic amount being sufficient. In fact, sulfide formation from **5** in the presence of 0.1 mol of **2** proceeds smoothly. Reaction of alkoxide ion with **5** proceeds via substitution at C-2 of the dithiole ring analogous to that of R^0S^- with **5**. The different reactive site between R^0S^- and R^1O^- can best be interpreted in terms of the soft base (R^0S^-)–soft acid (thion carbon of **5**) and hard base (R^1O^-)–hard acid (C-2 carbon of **5**) correspondence in the HSAB principle.[12]

The reaction between **1** and **2** is summarized stoichiometrically as follows. The solvent effect in this reaction can be explained by solvation of the nucleophile which depends on the dielectric constant (21.5 for acetone and 37.5 for acetonitrile). Poorer solvation of nucleophile (xanthate anion) in acetone in comparison to that in acetonitrile results in higher reactivity of the former system. This tendency can be also observed in the N_+ parameters defined by Ritchie.[13] If we compare the nucleophilicity of a given nucleophile in different solvents, confining the comparison to that of N_+ values in dipolar aprotic solvents, then the larger the N_+ values are, the smaller the dielectric constants, i.e., the lesser the solvation the larger N_+ value and the greater the nucleophilicity.

Table II. Rate Constants for the Decomposition of 8 Obtained from Figure 3 with $dx/dt/(a - x) = k_0 + k_2x^2$

Run no.	R_1	R_2	R_3	Solvent	Temp, °C	Concn, $\times 10^5$ M	k_0, $\times 10^4$ s^{-1}	k_2, $\times 10^{-5}$ M^{-2} s^{-1}
1	H		Morpholino	EtOH	25.4	6.46	1.47	1.19
2	H		Morpholino	EtOH	32.0	4.86	3.13	4.62
3	H		Morpholino	EtOH	38.6	6.15	5.03	5.69
4	H		Morpholino	MeCN	38.0	7.69	0.539	0.819
5	H		Morpholino	MeCN	44.5	6.12	1.15	2.08
6	H		Morpholino	MeCN	49.0	4.65	1.93	6.04
7	OMe		Morpholino	MeCN	44.5	4.47	1.45	4.78
8	Br		Morpholino	MeCN	44.5	8.14	0.865	0.829
9	H	Me	Ph	EtOH	52.5	4.22	1.07	1.74
10	H	Me	*p*-MeOPh	EtOH	52.5	6.72	0.870	0.486
11	Br	Me	Me	EtOH–MeCN	50.0	3.68	2.19	6.15
12	Cl	Me	Me	(9:1 v/v)	50.0	3.68	2.33	6.40
13	Me	Me	Me	EtOH–MeCN	50.0	3.68	3.80	9.69
14	OMe	Me	Me	EtOH–MeCN	50.0	3.68	7.54	17.6
15	OH	Me	Me	EtOH–MeCN	50.0	3.68	5.38	16.1

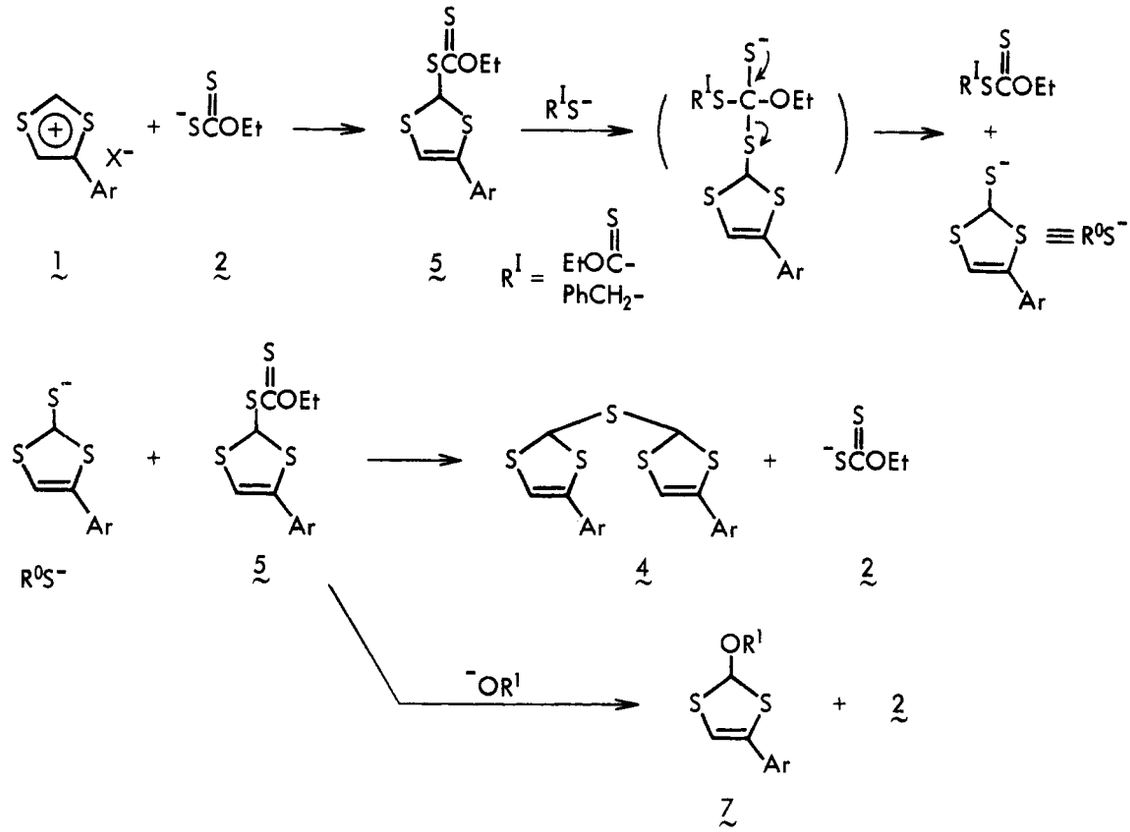


Figure 4. Reaction pathway for the formation of sulfide (4) from the reaction of 1 with 2.

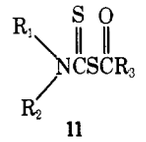
Table III. Activation Parameters for the First-Order Decomposition of 8

Solvent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
EtOH	16.5	−21.5
MeCN	22.0	−6.11

Decomposition of 8. Many studies have been made on the mechanism of acid- or base-catalyzed decomposition of dithiocarbamate salt[14] and base-catalyzed decomposition of thiolcarbonate or xanthate esters.[15] However, no attempt has been made to explain the mechanism of decomposition of dithiocarbamate esters, except for the acyl esters.[6,7]

There are three mechanisms that can be considered to explain the decomposition mechanism of 8, that is, (a) cyclic four-membered ring transition state, (b) stepwise mechanism, and (c) simultaneous two-bond heterolysis mechanism (Figure 5).

Decomposition of dithiocarbamate acyl esters (11) proceeds via pathway a, and the presence of an electron-withdrawing



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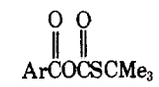
group attached to the acyl carbon, which makes it more positive, accelerates the decomposition. In this case, decomposition takes place via intramolecular nucleophilic attack of the amine moiety. The reverse is the case with the substituent effect of the decomposition of 8. Rate enhancement of the decarboxylation of thiolcarbonic carboxylic anhydride (12) is observed in polar solvent,[16] but the rate ratio does not vary largely with the polarity. Furthermore, the $\Delta S^{\ddagger}$ value of the



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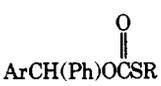
decarboxylation of 12 is large negatively with increase in solvent polarity. These facts indicate that the decomposition of 11 and 12 proceeds via path a, and the difference in $\Delta S^{\ddagger}$ due to the alternation of solvent polarity is due to that in the solvation of the incipient species. The rate of the decomposition of 8 is slower in the more polar solvent, MeCN, than in EtOH and the $\Delta S^{\ddagger}$ is more negative in the less polar but more powerful ionizing solvent, EtOH, than in MeCN. This result is the reverse of that of 12. Accordingly, mechanism a can be ruled out for the decomposition of 8.

Mechanism b proceeds via the heterolysis of 8 into the dissociated ion pair and the dithiocarbamate anion (2) formed further decomposes into CS_2 and $N^{-}R_2R_3$. Acid-catalyzed decomposition of 2 or xanthate anion has been described to proceed via the corresponding acid, and not the anion.[14] Protonation occurs between S and X (O or N) in the transition state. The dithiocarbamate anion is stable and no crossover product has been found for the decomposition of 8. From these results, we can conclude that the decomposition of 8 does not proceed via mechanism b.

Noncatalyzed decomposition of aralkyl thiocarbonate (13)



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is accelerated in a solvent having strong ionizing power,[17] and the plot of log k vs. pK_a (pK_a of mercaptans) deviates from a linear relationship with a decrease in pK_a. This fact shows that in the transition state, both C–O and C–S bonds cleave, the degree being smaller for the latter. Solvent dependence of the decomposition rates of 8 is the same as that of 13. From

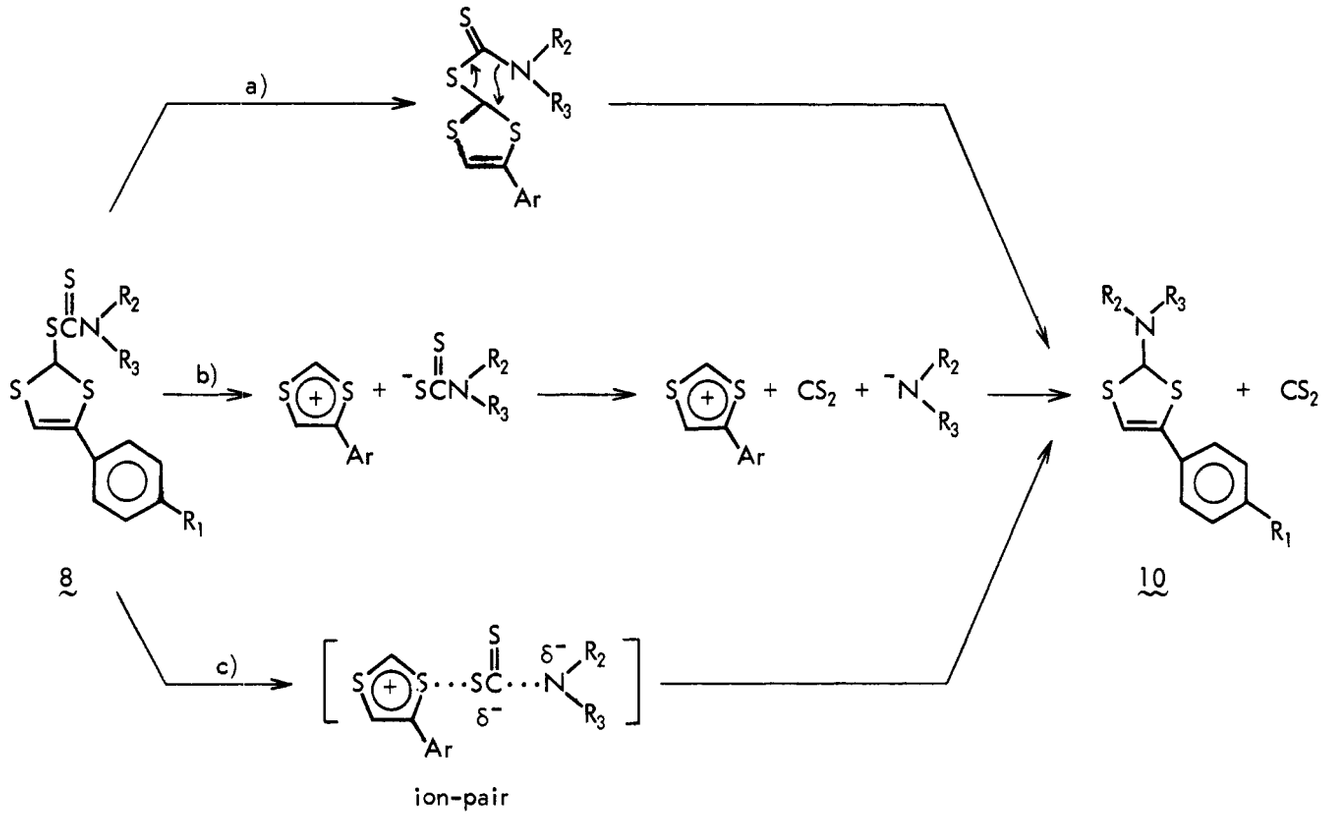

Figure 5. Three possible mechanisms for the thermal decomposition of dithiocarbamate ester (8) into aminodithiole (10) and CS_2.

these consideration, we can conclude that the decomposition of 8 (with regard to k_0) proceeds via mechanism c. This is further supported by the presence of both substituent effects of R_2, R_3, and R_1.

Decomposition of 8 is accelerated in a solvent having strong ionizing power (EtOH) and the degree of dissociation of the C–S and C–N bonds is affected by the nature of the substituents. The enhanced reactivity of *N*-alkyl derivatives (runs 1–8 in Table II) in spite of the larger extent of dissociation of the C–N bond in the transition state of *N*-aryl derivatives (runs 9 and 10) is ascribed to the larger nucleophilicity of the former. On the other hand, the presence of the electron-donating group on nitrogen destablizes the developing negative charge resulting from dissociation of the C–N bond. This results in lesser dissociation of the *N*-methoxyphenyl derivative than that of the *N*-phenyl one. The difference in the decomposition rate between phenyl and *p*-methoxyphenyl derivatives is thus estimated by comparing the stabilizing effects of the developing negative charge from the electron-donating *p*-methoxyphenyl groups.

A linear relationship of the Hammett plot of the substituent effect of R_1 against σ^+ is obtained. The same correlation of the substituent effect on σ^+ has also been seen for pK_{R^+} of 1[18] and for the decomposition of *tert*-butyl arylperacetate with which decarboxylation proceeds via mechanism c.[19]

The difference in $\Delta S^{\ddagger}$ in EtOH and MeCN can be explained as that in the solvation for the charge-separated transition state. The degree of dissociation of the C–S and C–N bonds in EtOH was larger than in MeCN. The solvent was needed to stabilize the developed polar transition state in EtOH. Hence the large negative $\Delta S^{\ddagger}$ value in EtOH.

Thiocarbonate esters are reported to be subject to base-catalyzed decomposition, which is first order with respect to the base, and the reaction might be intermolecular.[15] With regard to the second-order catalytic term of the product, the electron-donating atoms of the product associate with the positive charge of 8, which stabilizes 8.

Experimental Section

Melting points are uncorrected. UV spectra were measured with a Hitachi EPS-2 spectrometer, NMR spectra with a Varian A-60 instrument in $CDCl_3$ with Me_4Si as an internal standard, and mass spectra with a Hitachi RMU-6E mass spectrometer.

Preparation of Cation. Starting cations (1, 4-aryl-1,3-dithiolium and 2-substituted amino-4-aryl-1,3-dithiolium perchlorates) were prepared by a method described previously.[20]

4-Phenyl-1,3-dithiol-2-yl Sulfide (4a). A mixture of 0.56 g (2.0 mmol) of **1a** and 0.64 g (5.0 mmol) of **2** in 20 mL of acetone was refluxed for 2 h, then concentrated in vacuo. The residue was partitioned between chloroform and water. The organic layer was separated, dried over sodium sulfate, and evaporated to give the crude product. Recrystallization from chloroform yielded 0.28 g of **4a**: mp 167–169 °C dec; yield 73%; NMR δ 6.32 (s, 1), 6.37 (s, 1), 7.20–7.50 (m, 5, ArH); UV λ_{max} (EtOH) 232.5 nm (log ϵ 4.40), 255 (sh, 4.21), 314 (4.04), 345 (sh, 3.86); mass spectrum *m/e* 356 [15%, bis(4-phenyl-1,3-dithioledene), 210 (35%, 2-thioxo-4-phenyl-1,3-dithiole), 180 (79%, 4-phenyl-1,3-dithiole), 179 (100%, 4-phenyl-1,3-dithiolium cation), 134 (69%, phenylthirene), 121 (18%, thiobenzoyl cation), 102 (85%, phenylacetylene), 89 (19%), 77 (14%, Ph or CS_2H^+), 45 (21%, CSH^+).

Anal Calcd for $C_{18}H_{14}S_5$: C, 55.34; H, 3.61; S, 41.05. Found: C, 55.82; H, 3.57; S, 40.81.

An authentic sample of **4a** was prepared as follows. To an ice-cooled solution of 0.36 g (1.5 mmol) of sodium sulfide nonahydrate in 5.0 mL of water was added 0.84 g (3.0 mmol) of **1a** with efficient stirring. The mixture was stirred for 1 h, then extracted with chloroform. The chloroform layer was dried over sodium sulfate, then evaporated to give 0.39 g (66%) of **4a**, the IR spectrum of which was identical with that for the product obtained in the above reaction.

Treatment of a small amount of **4a** with aqueous $HClO_4$ in acetronitrile gave the characteristic odor of hydrogen sulfide. Addition of excess ether gave a colorless precipitate with an IR spectrum identical with that of **1a**.

***S*-4-Phenyl-1,3-dithiol-2-yl *O*-Ethylxanthate (5a).** To a solution of 0.56 g (2.0 mmol) of **1a** in 10 mL of acetonitrile was added 0.32 g (2.5 mmol) of **2** at room temperature. The mixture was stirred for 2 h, then filtered. The filtrate was concentrated and excess ether was added. The precipitate which formed was filtered off, then concentrated to give 0.58 g (97%) of **5a** as an oil: NMR δ 1.43 (t, 3, Me), 4.66 (q, 2, CH_2), 6.40 (s, 1), 7.50–7.17 (m, 5, ArH); UV λ_{max} (EtOH) 231 nm (log ϵ 4.09), 240 (sh, 4.02), 307 (3.92), (CH_3CN) 227 (4.27), 245 (sh, 4.14), 283 (4.07), 330 (3.78).

Anal. Calcd for $C_{12}H_{12}OS_4$: C, 47.96; H, 4.03; S, 42.68, Found: C, 47.81; H, 4.01; S, 42.74.

By the same method, **5b** was obtained as an oil: yield 91%; NMR δ 1.43 (t, 3, Me), 4.67 (q, 2, CH_2), 6.41 (s, 1), 6.68 (s, 1), 7.30 (s, 4, ArH).

Anal. Calcd for $C_{12}H_{11}ClOS_4$: C, 43.03; H, 3.31; S, 38.30; Cl, 10.58. Found: C, 43.30; H, 3.41; S, 38.18; Cl, 10.86.

Reaction of 5a with 2. A solution of 0.78 g (2.9 mmol) of **5a** in 25 mL of acetone was refluxed for 2 h. TLC showed the presence of **5a** only at this stage. To this solution 0.032 g (0.25 mmol) of **2** was added, and the mixture was refluxed for a further 3 h, then allowed to stand overnight. The reaction mixture was concentrated to dryness and the residue was partitioned between chloroform and water. Workup as described in the reaction between **1a** and **2** in acetone yielded 0.37 g (73%) of **4a**, which was confirmed by comparing the IR spectrum with that of an authentic sample.

By the same method, **4b** was obtained in 64% yield after recrystallization from chloroform: mp 153–155 °C; NMR δ 6.30 (s, 1), 6.37 (s, 1), 7.32 (s, 4, ArH); UV λ_{max} (EtOH) 244 nm (log ϵ 4.34), 323 (4.17).

Anal. Calcd for $C_{18}H_{12}Cl_2S_5$: C, 47.05; H, 2.63; S, 34.89; Cl, 15.43. Found: C, 47.36; H, 2.60; S, 34.70; Cl, 15.27.

Reaction of 5a with Benzyl Mercaptide. To an ice-cooled solution of 0.25 g (5.0 mmol) of sodium hydroxide in 25 mL of acetonitrile was added 0.62 g (5.0 mmol) of benzyl mercaptan. The mixture was stirred for 5 min, then 1.50 g (5.0 mmol) of **5a** in 10 mL of acetonitrile was added. Stirring was continued for 3 h with ice cooling. Then the mixture was concentrated and partitioned between chloroform and water. Undissolved material was filtered off to give 0.12 g of **4a**. The organic layer was concentrated and the residue was washed with ether, the residue being 0.47 g of **4a**. The filtrate was again concentrated and the residue was washed with *n*-hexane. Here 0.082 g of **4a** (for a total 0.67 g of **4a**) was separated. Evaporation of the solvent afforded 0.60 g of *S*-benzyl *O*-ethylxanthate (**6**) as an oil: NMR δ 1.38 (t, 3, Me), 4.64 (q, 2, CH_2), 4.36 (s, 2, CH_2), 7.28 (s, 5, ArH).

An authentic sample of **6** was prepared as follows.[21] A mixture of 0.63 g (5.0 mmol) of benzyl chloride and 0.80 g (5.0 mmol) of potassium xanthate in 15 mL of acetonitrile was stirred for 1 h at room temperature; then the mixture was concentrated and the residue partitioned between ether and water. Concentration of the ether solution gave 0.93 g of ester (**6**), which was identified by spectral comparison with the above product.

Reaction of 5a with Alkoxide. To a solution of 0.046 g (2.0 mmol) of sodium in 5.0 mL of ethanol was added 0.60 g (2.0 mmol) of **5a**. The reaction mixture was refluxed for 1.5 h, then allowed to stand overnight. The residue obtained from evaporation of the solvent was partitioned between chloroform and water. The organic layer was separated, dried over sodium sulfate, and concentrated to yield 0.32 g (72%) of 2-ethoxy-4-phenyl-1,3-dithiole (**7**) as an oil. The identity of **7** was confirmed by comparing its spectra with that of an authentic sample.[3]

By using methanol instead of ethanol the 2-methoxy derivative of **7** was obtained in 94% yield (oil).

Sodium Dithiocarbamate (3). N,N-Disubstituted dithiocarbamates were prepared by the method of Heyningen and Brown.[22]

***S*-(4-Aryl-1,3-dithiol-2-yl) N,N-Disubstituted Dithiocarbamate (8).** The general procedure for synthesis of **8** has been described.[3] The results are summarized in Table I.

Reaction of 8a with Piperidine. A mixture of 599 mg (2.0 mmol) of **8a** and 340 mg (2.0 mmol) of piperidine in 20 mL of EtOH was stirred for 2.5 h at room temperature. The solvent was removed in vacuo and the residue was dissolved in ether, washed with water, separated, and dried. Concentration of the solvent, followed by recrystallization from EtOH, yielded 320 mg (80%) of 2-piperidino-4-phenyl-1,3-dithiole (**10a**), mp 87–88 °C. The IR of the product agreed with that of the authentic sample.[20]

Reaction of 8a with Sodium Piperidinodithiocarbamate (3). A solution of 599 mg (2.0 mmol) of **8a** and 876 mg (2.0 mmol) of **3** dihydrate in 20 mL of EtOH was stirred for 2 h at 50 °C, then concentrated. The residue was extracted with AcOEt, washed with water, separated, and dried. The solvent was removed in vacuo, and the residue was washed with ether to afford 297 mg (44%) of *S*-(4-phenyl-1,3-dithiol-2-yl)piperidinodithiocarbamate (**8l**), which had an IR spectrum identical with that of the authentic sample (see Table I).

Thermolysis of 8 into 10. Thermolysis of 8l. A suspended solution of 340 mg of **8l** in 10 mL of EtOH was stirred for 2 h at 60 °C, then concentrated in vacuo. The residue was triturated with ether. The residue was separated by filtration to give 137 mg (40.5%) of undecomposed **8l**. Evaporation of filtrate afforded 152 mg (57.5%) of 2-piperidino-4-phenyl-1,3-dithiole (**10a**), which had an IR spectrum identical with that of the authentic sample.[20]

Thermolysis of 8a. A solution of 300 mg of **8a** in 15 mL of methylene chloride was refluxed for 75 h. Evaporation of the solvent followed by washing with petroleum ether and recrystallization from EtOH gave 215 mg (96.5%) of 2-dimethylamino-4-phenyl-1,3-dithiole (**10b**). The structure of the product was confirmed by comparing its spectral data with those of the authentic sample.[20] Thermolysis of **8a** in EtOH (the same conditions as for **8l**) gave 83% decomposed product.

Kinetics. Decomposition of **8** was characterized by a decrease in absorption due to substrate at 267 nm and a simultaneous growth in absorption at 315 nm characteristic of the decomposed product, with isosbestic points at 304 and 325 nm being maintained throughout the course of decomposition. The rate of decomposition was determined spectrophotometrically at 257 nm. Rate constants were then calculated from the plot of

$$dx/dt/(a - x) \text{ vs. } x^2$$

where a is the initial quantity of **8** and x is the quantity of the product (**10**) at time t. Usually, the plot of x vs. t gave a straight line (< about 75% decomposition), and $dx/dt = x/t$ was approximated. Because the decomposition of **8** takes place immediately after its contact with solvent, the initial absorbance was estimated graphically from the plot of absorbance vs. t, and the absorbance of the product at time infinity was obtained by allowing the sample to stand overnight.

Registry No.—**1a**, 24396-11-0; **1b**, 24372-89-2; **2**, 140-89-6; **3**, 873-57-4; **4a**, 61522-70-1; **4b**, 61522-71-2; **5a**, 61522-72-3; **5b**, 61522-73-4; **6**, 2943-26-2; **8a**, 24395-63-9; **8b**, 61522-74-5; **8c**, 61522-75-6; **8d**, 61522-76-7; **8e**, 61522-77-8; **8f**, 61522-78-9; **8g**, 61522-79-0; **8h**, 61522-84-7; **8i**, 61522-80-3; **8j**, 61522-81-4; **8k**, 61522-82-5; **8l**, 24395-62-8; **8m**, 24395-13-9; **8n**, 61522-83-6; **8o**, 61522-85-8; **8p**, 61522-86-9; **8q**, 61522-87-0; **8r**, 61522-88-1; **8s**, 61522-89-2; **8t**, 61522-90-5; **9a**, 61522-91-6; **9b**, 61522-92-7; **9c**, 61522-94-9; **9d**, 61522-96-1; benzylmercaptide, 100-53-8; sodium ethoxide, 141-52-6; piperidine, 110-89-4.

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Dipole Moment, Nuclear Magnetic Resonance, and Infrared Studies of Phosphorus Configurations and Equilibria in 2-R-2-Oxo-1,3,2-dioxaphosphorinanes

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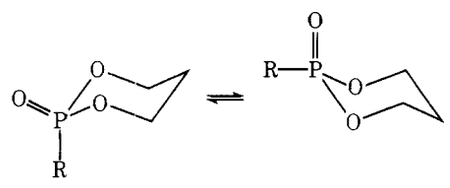
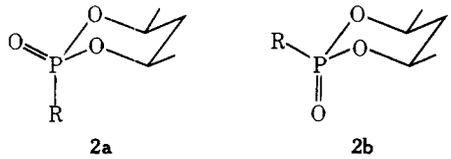
Substantial dipole moment differences (1.3–2.2 D) permit assignment of the stereochemistry at phosphorus in isomeric pairs of 2-R-2-oxo-4,6-dimethyl-1,3,2-dioxaphosphorinanes wherein R = Me (**3a,b**), H (**4a,b**), OMe (**5a,b**), and NMe_2 (**6a,b**) where **a** and **b** denote axial R (equatorial P=O) and equatorial R (axial P=O) relationships, respectively. Analogous assignments were obtained from similar measurements on the isomeric pairs of 2-R-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes wherein R = Me (**7a,b**), H (**8a,b**), OMe (**9a,b**), and NMe_2 (**10a,b**). LIS experiments on **7–10** confirm these assignments. The **a** isomers of **3, 5, 6** and **7, 9, 10** exhibit $\delta^{31}P$ values upfield of those of the **b** isomers whereas the opposite is true for **4a,b** and **8a,b.** Doubling (ca. 19 cm^{-1}) of the phosphoryl stretching frequencies in **5b** and **9b** is attributed to rotational isomerism of the MeO groups while the lack of such doubling in the **a** isomers is attributed to steric restrictions. A more pronounced doubling (ca. 40 cm^{-1}) of this frequency in **6a** and **10a**, on the other hand, may be due to the presence of a second conformer arising as a result of the severe 1–3 steric interactions. The μ and $\delta^{31}P$ values and the extinction coefficients of the P=O stretching frequencies associated with **a** and **b** isomers of the rigid-ring model compounds **3–6** were compared to those of the analogous compounds which were free to attain conformational equilibrium by virtue of the absence of the 4,6-dimethyl substituents. All the data are in accord with a substantial axial R (equatorial P=O) group preference when R = H and MeO, although this preference is slightly reversed for R = Me and strongly opposite when R = Me_2N at room temperature in benzene.

Phosphorus stereochemistries and ring conformations of phosphorinanes, especially the 1,3,2-dioxaphosphorinanes reported here, have received considerable attention in recent years. Several instrumental techniques have been employed, from which conflicting conclusions have been occasionally drawn (vide infra). The purpose of this paper is to report a new approach to the use of solution techniques which eliminates some of the ambiguities.

The investigations reported in the literature for 2-R-2-oxo-1,3,2-dioxaphosphorinanes fall into two broad categories: (1) studies of phosphorus configurations and ring conformational equilibria of conformationally mobile systems such as **1**, and (2) assignments of phosphorus configurations of rings with conformationally reduced mobility such as **2a** and **2b.** It



1



2a **2b**

should be noted that 5,5-dimethyl derivatives are not expected to influence the mobility significantly and they are therefore in the same class with **1.** On the other hand, 4-methyl and 5-*tert*-butyl substituted rings resemble **2** in being more conformationally rigid.

Five instrumental techniques (^1H NMR, ^{13}C NMR, ^{31}P NMR, infrared, and dipole moment experiments) have been used for determinations of phosphorus stereochemistries and ring conformations in solution as is briefly outlined below.

Coupling constants among ring hydrogens and between phosphorus and ring protons have been found to be valuable both for conformer distribution determinations in type **1** compounds and for phosphorus stereochemical assignments.[1] Thus, it has been reported that $^3J_{POCH_{eq}}$ coupling constants are larger for compounds with equatorially oriented substituents in trivalent 1,3,2-dioxaphosphorinanes than for the axial analogues.[2] However, this criterion has been incorrectly applied to 2-oxo analogues[3] which in fact do not exhibit such behavior.[4] Because of this problem in 2-oxo compounds, lanthanide induced shift (LIS) experiments on protons in the molecule become very useful. Mosbo and Verkade have demonstrated that the C4 and C6 axial protons are shifted considerably further downfield in compounds with the **2b** configuration than in those with **2a.**[5] Dale[6] has reported conformer distributions determined from type **1** compounds employing LIS experiments, but the results must be viewed with caution since Bentrude and co-workers[7] have found that the presence of a lanthanide shift reagent can cause conformational changes.

The use of ^{13}C NMR spectra has been reported in only a few instances to identify type **2** isomers. It has been demonstrated that the chemical shift of a carbon atom γ to an axial phosphorus substituent (**b** isomer) is upfield of the **a** isomer.[2b,c]