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Iminodithiocarbonates. III.[1] Reactions with Some Electrophiles and the Structural Effect on Nucleophilic Reactivities and Basicities[2]

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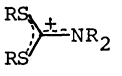
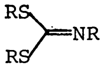
With a view toward demonstrating the structural effect on the reactivity of iminodithiocarbonates, the reactions of some electrophilic reagents with the following four iminodithiocarbonates have been studied; 2-methylimino-(IVa) and 2-phenylimino-1,3-dithiolane (IVb) and *S,S'*-dimethyl-*N*-methyl-(Va) and *S,S'*-dimethyl-*N*-phenyliminodithiocarbonate (Vb). Cyclic IVa and its *N*-ethyl homologue reacted with an equimolar amount of phenyl isocyanate at room temperature giving 1:2 cycloadducts. However, the other imino compounds (IVb, Va, and Vb) did not react at all even at elevated temperature. All these imino compounds reacted with acid chlorides to afford the corresponding *N*-acyliminium salts which could, in some cases, be isolated; however the rate of formation of the salts varied significantly with the structure of the imino compound. Some reactions with alkyl halides and phenyl isothiocyanate were also attempted. From the present results and those previously obtained on their reactions with epoxides and with ketenes, it has been concluded that the nucleophilic reactivity of the imino compounds increases in the order Vb<Va<IVb<IVa. Furthermore, it was found that the basicity of the imino compounds increased in the order Vb<IVb<Va<IVa. The observed ring effect and *N*-substituent effect on the reactivity and basicity of the imino compounds are discussed in connection with similar effects on the stability of closely related tri(hetero)carbonium ions, *i.e.*, bis(alkylthio)-dialkylaminocarbonium ion (I).

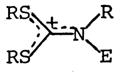
In our previous paper on tri(hetero)-substituted carbonium ions,[3-5] we reported that the electrophilic reactivity of tri(hetero)substituted carbonium ions (I) depends upon their structural factors, *e.g.*, whether they are cyclic or open-chain. On the other hand, the reaction of iminodithiocarbonates (II) with an electrophile ($^{+}$E) should involve an initial formation of tri(hetero)-substituted carbonium ions (III). Thus it could be expected that the nucleophilic reactivity of



I



II



III

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[1] Part I: Y. Ueno, T. Nakai, and M. Okawara, This Bulletin, **43**, 162 (1970), Part II: Y. Ueno, T. Nakai, and M. Okawara, *ibid.*, **43**, 168 (1970).

[2] Presented in part at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969.

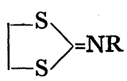
[3] T. Nakai, Y. Ueno, and M. Okawara, *Tetrahedron Lett.*, **1967**, 3831; This Bulletin, **43**, 156 (1970).

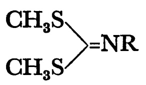
[4] T. Nakai and M. Okawara, *Tetrahedron Lett.*, **1967**, 3835; This Bulletin, **43**, 1864 (1970).

[5] T. Nakai, and M. Okawara, This Bulletin, **43**, 3528 (1970).

the imino compound (II) is closely related to the stability of the tri(hetero)carbonium ion formed (III).

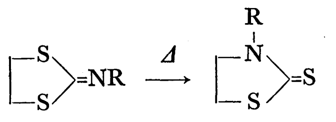
However, little information has been available on the reaction of II with electrophilic reagents although there are a few papers reporting the reaction of II with epoxides[6] and with ketenes.[7] In order to obtain more elaborate information on the structural effect on the nucleophilic reactivity of iminodithiocarbonates (II), reactions of various types of II with some electrophilic reagents have been studied. Iminodithiocarbonates studied are: 2-methylimino-(IVa) and 2-phenylimino-1,3-dithiolane (IVb) and *S*,*S*′-dimethyl-*N*-methylimino-(Va) and *S*,*S*′-dimethyl-*N*-phenyliminodithiocarbonate (Vb). Furthermore, the basicity of these imino compounds has been measured. In this paper we will describe the results of the investigation and discuss the structural effect on nucleophilic reactivity and basicity.


IVa, R$=CH_3$
b, R$=C_6H_5$

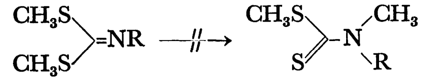

Va, R$=CH_3$
b, R$=C_6H_5$

Results

Thermal Isomerization. We reported that 2-methylimino-1,3-dithiolane (IVa) and *N*-ethyl homologue are ring-isomerized at 200°C to the corresponding thiazolidine-2-thione (VI), but 2-phenylimino compound (IVb) is not isomerized even under more drastic conditions.[6]

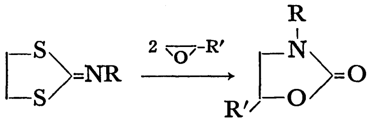

IV VI
R$=CH_3$, C_2H_5

Attempts to isomerize the open-chain compounds (Va and Vb) were made under various conditions. However, the two compounds were not isomerized to dithiocarbamates even at 250—270°C.


V
R$=CH_3$, C_6H_5

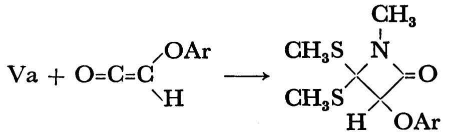
Harley-Mason has reported that *S*,*S*′-diphenyl-*N*-phenyliminodithiocarbonate remains unchanged on heating at 330°C.[8]

Reactions with Epoxides. We reported that the cyclic compounds (IVa and IVb) react with epoxides at 140—160°C to give the 2-oxazolidone derivatives (VII) in good yields and suggested that the initial process of this reaction is a cycloaddition of epoxides to the C=N bond of IV.[6,9]


IV VII
R$=CH_3$, C_6H_5

The reactions of open-chain Va and Vb with propylene oxide were carried out under various conditions. It was found that neither Va nor Vb reacted with epoxide even at 170—180°C, but the starting materials were recovered.

Cycloaddition Reactions with Heterocumulenes. Metzger reported that *o*-chlorophenoxyketene or diphenylketene reacts with numerous iminodithiocarbonates including 2-propylimino-1,3-dithiolane and open-chain Va to afford the corresponding 1:1 cycloadduct (VIII),[7] *e.g.*


VIII

The reactions of the four iminodithiocarbonates with phenyl isocyanate were attempted. It was found that methylimino-dithiolane (IVa) reacted with an equimolar amount of phenyl isocyanate at room temperature to produce the 1:2 cycloadduct (IXa) in 65% yield. Similarly, ethylimino-dithiolane (IVa′) and the isocyanate gave the 1:2 cycloadduct (IXa′) in 16% yield in the presence of a small amount of lithium chloride; however, in the absence of the catalyst no reaction proceeded appreciably. In contrast to this observation, the other iminodithiocarbonates (IVb, Va, and Vb) did not react with the isocyanate even at elevated temperature and the starting materials were recovered almost quantitatively.

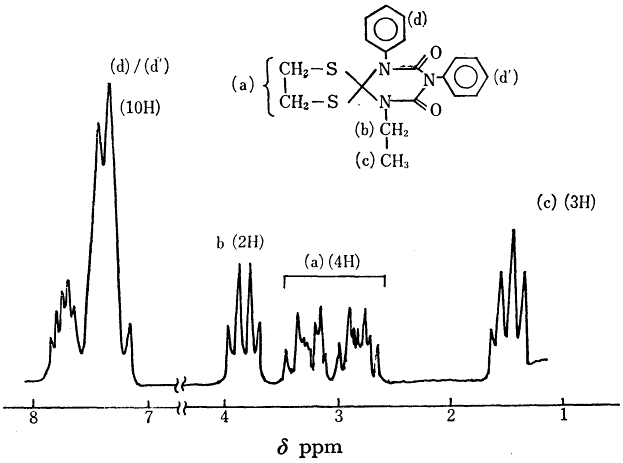


Fig. 1. The NMR spectrum of 1:2 cycloadduct IXa′ in $CDCl_3$

Products IXa and IXa′ were identified by means of elemental analyses and spectral data (IR and NMR). The IR spectra of IXa and IXa′ showed two strong absorption bands at 1703 and 1668—1670 cm^{-1} indicating the presence of two kinds of carbonyl groups. The structure of IXa′ was confirmed by the NMR spectrum (Fig. 1) which showed a triplet at δ 1.42

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[6] Y. Ueno, T. Nakai, and M. Okawara, *ibid.*, **43**, 162 (1970).

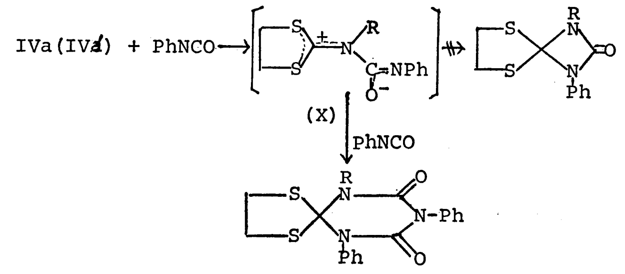
[7] C. Metzger, *Chem. Ber.*, **101**, 1120 (1968).

[8] J. Harley-Mason, *Nature*, **155**, 515 (1945).

[9] Y. Ueno, T. Nakai, and M. Okawara, This Bulletin, **43**, 168 (1970).

$(N\text{-}CH_2C\underline{H}_3)$, a quartet at δ 3.83 $(N\text{-}CH_2CH_3)$, two multiplets centered at δ 3.28 and 2.28 $(S\text{-}CH_2CH_2\text{-}S)$, and a multiplet centered at δ 7.45 (two phenyls). Unequivalence of the two ring-methylenes is noteworthy. It suggests that the phenyl nucleus would significantly deshield the methylene protons situated near the phenyl nucleus.

Product IXa is best explained as a result of an initial formation of the ionic 1:1 adduct (X) which then reacts with additional isocyanate, finally yielding the six-membered ring compound (IXa) instead of the formation of the more hindered four-membered 1:1 cycloadduct.



IXa, $R=CH_3$
a', $R=CH_3CH_2$

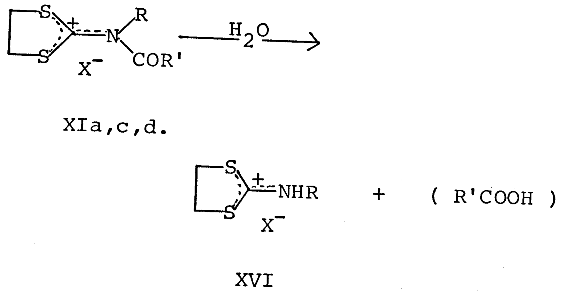
The formation of the 1:2 cycloadduct in equimolar condition is in direct contrast to the reaction of the isopropyl analog of IVa with ketenes described above, and to the reactions of mono-substituted azomethines with phenyl isocyanate only at elevated temperature giving six-membered 2:1 cycloadducts.[10]

Reactions of the four imino compounds with phenyl isothiocyanate were attempted; however, no significant reactions were observed.

Reactions with Acid Chlorides. The acylating reactions with acid chlorides have been carried out in the presence of tertiary amine. In these cases existance of acylammonium salts as reactive intermediates has been postulated. However, the acylammonium salts were so unstable that only a few salts have been successfully isolated. Acyliminium salts such as acylpyridinium salt are also too unstable to be isolated.

If the iminodithiocarbonates reacts with an acid chloride, the acyliminium salt formed would be greatly stabilized through delocalization of the positive charge by the two sulfur atoms as shown below.

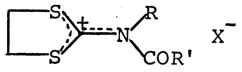
Reactions of imino-dithiolane IVa and IVb with acetyl chloride, benzoyl chloride, and methacryloyl chloride were carried out at room temperature in inert solvents such as ether or benzene. The reaction proceeded immediately to completion yielding crystalline adducts XI quantitatively. In the reaction of IVa with acetyl chloride it was necessary to cool the reaction mixture with dry ice-acetone bath because of violent heat evolution. On the other hand, in the reaction of IVb with benzoyl chloride, the reaction proceeded slowly. The acyliminium salts obtained were stable white solids in inert solvent, but they were hygroscopic in air. An exchange of the counter anion of Cl^- with $SbCl_6^-$ or $B(C_6H_5)_4^-$ was successful in the case of XIb and XIe. However, in other cases, the salts were easily hydrolyzed giving rise to the formation of HX salts of iminodithiocarbonates, XVI.



XIa,c,d.

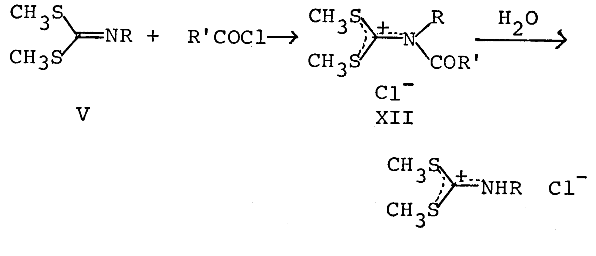
XVI

Table 1. *N*-Acyliminium salts XI



	R	R'	X	IR (KBr) ($\nu_{C=O}$) cm^{-1}	Mp (°C)
XIa	CH_3	CH_3	Cl	—	—
b	CH_3	C_6H_5	Cl	1700	126—129
b'	CH_3	C_6H_5	$SbCl_6$	1700	134—135
c	C_6H_5	CH_3	Cl	—	—
d	C_6H_5	C_6H_5	Cl	—	—
e	CH_3	$CH_2=\underset{CH_3}{\underset{\mid}{C}}$	$B(C_6H_5)_4$	1740	110

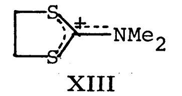
Similarly, open-chain iminodithiocarbonates Va and Vb reacted with acetyl chloride to give very hygroscopic *N*-acethyliminium chlorides (XII) which were easily hydrolyzed with the moisture in air.



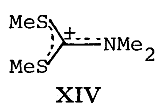
V

XII

Stability of N-*Acyliminium Salts (XI, XII).* Cyclic iminium salts XI were more stable than open-chain analogs XII. This is in agreement with the fact that 2-dimethylamino-1,3-dithiolanium salt XIII in more stable than its open-chain analog XIV.[12]



XIII



XIV

XIb and XIe in particular, were stable enough to be isolated and characterized by IR spectra and elemental analyses.

Thus, stabilization of XI is increased by the *N*-sub-

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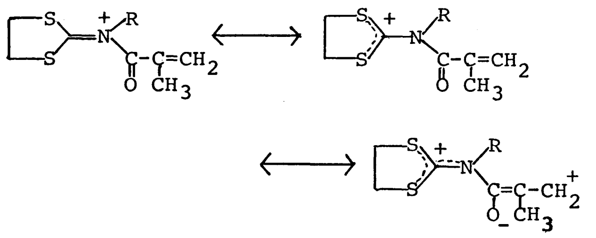
10) H. Ulrich, "Cycloaddition Reactions of Heterocummulenes," Academic Press, New York (1967), pp. 153—155.

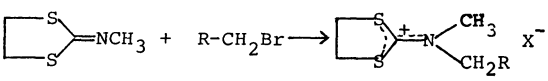
stituent in the order $CH_3<C_6H_5<CH_2{=}\underset{CH_3}{\underset{|}{C}}$–.

This was rationalized by the following resonance effect, which caused the decrease in the positive charge on the nitrogen atom.



Acylation of Amine by N-*Acyliminium Salt XI.* The strong acylating ability of the *N*-acyliminium salt XI was demonstrated using the IVb acetyl chloride adduct, XIc. The solution of aniline in benzene was added to the suspension of XIc in the same solvent and the mixture was warmed in a water-bath for one minute to produce acetanilide in 52% yield.

Reactions with Alkyl Halides. Alkylation of imino-1,3-dithiolane IVa with active halides such as α-haloketone, α-haloester and benzyl halide easily took place, producing the *N*,*N*-dialkyliminium salts XV in acetonitrile or under neat conditions at room temperature. Thus, IVa reacted with phenacyl bromide, ethyl bromoacetate and *p*-nitrobenzyl bromide to give the iminium salts XVa, b, and c in 92, 93, and 92% yield, respectively.



XVa, $R{=}C_6H_5CO$ $X{=}ClO_4$
b, $R{=}EtOCO$ $X{=}ClO_4$
c, $R{=}p\text{-}NO_2C_6H_4$ $X{=}Br$

In the case of XVa and XVb, the counter anion was exchanged into perchlorate anion by treating the salts with sodium perchlorate. Similarly, methylation of IVa with methyl iodide occurred to produce 2-dimethylamino-1,3-dithiolanium salt XIII in good yield.

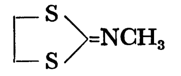
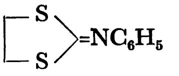
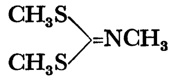
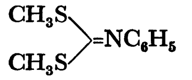
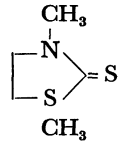
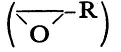
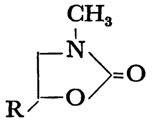
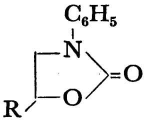
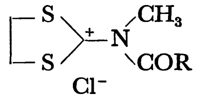
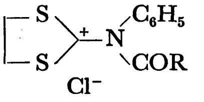
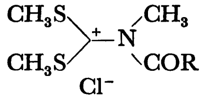
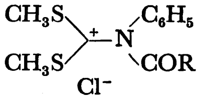
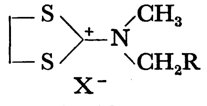
On the other hand, 2-phenylimino-1,3-dithiolane (IVb) or *S*,*S'*-dimethyl-*N*-methyliminodithiocarbonate (Va) reacted with phenacyl bromide to give unidentified products and no simple alkylation products were obtained.

Determination of the Basicities of the Iminodithiocarbonates (IV and V) by Spectrophotometry. Basicities of IV and V were calculated using the following equation,[11]

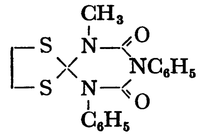
$$pK_a = pK_{HAc} + \log(C_{Ac^-}/C_{HAc}) + \log(D-D_{B^-}/D_{HB}-D)$$

where D_{B^-}, D_{HB}, and D refer to the absorption coefficient of the iminodithiocarbonates measured in water

TABLE 2. NUCLEOPHILIC REACTIVITIES OF IMINODITHIOCARBONATES

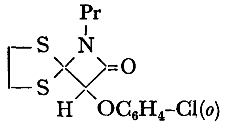
Reactants[g]				
p*K*a	5.2	3.2	4.8	2.7
Thermal isomerization		← N.R.[a] →		
Epoxide 			← N.R. →	
C_6H_5NCO	1:2 adduct[b]	← N.R. →		
C_6H_5NCS	← N.R. →			
RCOCl				
RCH_2X		d)	d)	——
Ketene[c]	1:1 adduct[e]	——	1:1 adduct[f]	

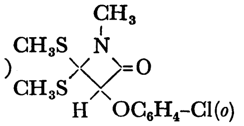
a) no reaction

b) 

c) C. Metzger, *Chem. Ber.*, **101**, 1120 (1968).

d) unidentified products

e) 

f) 

g) The respective reactions were carried out under similar conditions.

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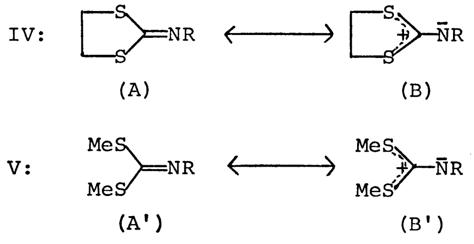
[11] L. P. Hammet. L. A. Flexser, and A. Dingboll, *J. Amer. Chem. Soc.*, **57**, 2103 (1935).

(curve 1), in aqueous sulfuric acid (curve 2), and in acetic acid-sodium acetate buffer solution (curve 3), respectively. For the calculation, values of D_{B^-}, D_{HB}, and D were taken from the curves 1, 2, and 3, respectively, at some wave lengths omitting than those in the neighborhood of the isobestic point. The value of p*K*a of acetic acid was taken as 4.76. Complete protonation of IVa was observed in over 18.2 wt% of aqueous sulfuric acid. The values of p*K*a of IVb, Va, and Vb were calculated in a similar manners. The p*K*a values are summarized in Table 2.

Correlation between Nucleophilic Reactivities and Structures of Iminodithiocarbonates. The nucleophilic reaction data of the iminodithiocarbonates including the previous results[6] are summarized in Table 2. We see that 1) nucleophilic reactivites of iminodithiocarbonates decrease in the order IVa>IVb>Va>Vb, and 2) this order is almost in agreement with that of basicities of the imino groups.

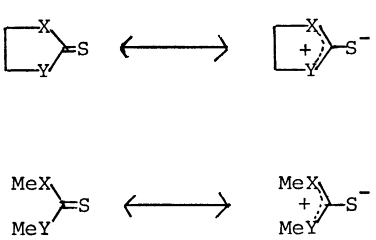
These observations indicate that the nucleophilic reactivities of iminodithiocarbonates may qualitatively be explained in terms of the basicities of the imino groups.

Ring Effect. The greater reactivities and basicities of cyclic IV than those of open-chain V show that the polarized structure (B) significantly contributes to the ground state of the former, and that the structure (B′) in the latter is less important.



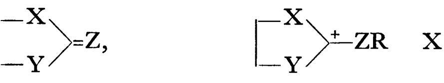
In other words, resonance stabilization of the polarized structure (B and B′) by the two sulfur atoms is greater in cyclic than open-chain analog.

A similar ring effect was observed in the greater basicities and reactivities toward epoxides of various cyclic thione compounds than in those of open-chain analog.[9]



X,Y=O,S,NR

Moreover, the ring effect has also been observed in the stability of tri(hetero)substituted carbonium ion; thus cyclic cation XIII was more stable than open-chain analog XIV.[12] This is also true for the stability of *N*-acyliminium salts. In general, ring effects such as enhanced reactivity, basicity, and stability of the cyclic compounds might be recognized in the following compounds as compared with open-chain analogs.



(X, Y, Z=O, S, NR′)

The ring effect is probably attributed to a much greater overlap between the lone pairs of the heteroatoms and 2*p* orbital of sp^2 center carbon in the ring compounds than in the analogous open-chain compounds.

N-*Substituents.* In both cases of IV and V, the difference of p*K*a between the *N*-methyl and the *N*-phenyl derivatives is 2.0—2.1. This shows that a pair of electrons on the iminonitrogen of IV and V are delocalized over the phenyl nucleus to the same extent. Thus the smaller reactivities of *N*-phenyl derivatives can be explained by this electron delacalization. In summary, the nucleophilic reactivities of iminodithiocarbonates are explained in terms of the ring effect and the *N*-substituents.

Experimental

General. All melting and boiling points are uncorrected. IR and UV spectra were recorded with Hitachi EPI-S-2 and EPS-2 spectrometers, respectively. NMR spectra were obtained with a Japan Electron Optics JNL 4H-100 spectrometer. Chemical shifts are given in ppm from tetramethylsilane as an internal standard.

Materials. All iminodithiocarbonates were prepared by the methods previously reported: methylimino-1,3-dithiolane (IVa), bp 79—81°C/0.45 mmHg; ethylimino-1,3-dithiolane (IVa′), bp 85—87°C/0.30 mmHg; phenylimino-1,3-dithiolane (IVb), mp 47—48°C; *N*-methylimino-dithiocarbonate (Va), bp 110—112°C/70 mmHg; *N*-phenylimino-dithiocarbonate (Vb), mp 34—35°C. Other reagents were either commercially available materials or prepared by a standard method.

Reaction of Methylimino-dithiolanes with Phenyl Isocyanate. Methylimino-dithiolane IVa (1.3 g, 0.01 mol) and phenyl isocyanate (1.2 g, 0.01 mol) were mixed at room temperature. A vigorous exothermic reaction occurred and crystals were immediately formed. After standing the reaction mixture at room temperature overnight, the precipitates were collected by filtration to give 1.2 g (65%) of the 1:2 cycloadduct (IXa). To remove the impurities (diphenylurea), the precipitates were washed several times with warm ether and recrystallized from acetonitrile: mp 231.5—232.5°C; IR (KBr) 1703 and 1670 cm^{-1} (C=O).

Found: C, 58.34; H, 4.39; N, 11.53%. Calcd for $C_{18}H_{17}N_3O_2S_2$: C, 58.22; H, 4.61; N, 11.32%.

The reaction of imino-dithiolane IVa′ with phenyl isocyanate was carried out under similar conditions in the presence of lithium chloride (0.10 g) to produce the cycloadduct IXa′ in 16% yield: mp 202—203°C (recrystallized from a mixture of ethanol and ether): IR (KBr) 1703 and 1668 cm^{-1} (C=O),

Found: C, 59.01; H, 5.00; N, 10.94%. Calcd for $C_{19}H_{19}N_3O_2S_2$: C, 59.21; H, 4.97; N, 10.90%.

The IR spectrum of IXa′ closely resembled that of IXa. The NMR spectrum of IXa′ is given in Fig. 1.

Reaction of Iminodithiocarbonates (IV or V) with Acid Chlorides. General Procedure: The iminodithiocarbonate was mixed with the acid chloride listed in Table 1 at room temperature in inert solvent (benzene, ether) or under neat conditions. Acyliminium salts were obtained as crystalline solids.

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

Reaction of Imino-dithiolane IVa with Benzoyl Chloride. IVa (1.3 g, 0.01 mol) and benzoyl chloride (1.4 g, 0.01 mol) were mixed. A white crystalline precipitate XIb started to separate almost immediately. The acyliminium salt XIb was obtained in quantitative yield, mp 126—129°C (recrystallized from benzene); IR (KBr): 1700 cm^{-1} (C=O).

Found: N, 5.12%. Calcd for $C_{11}H_{12}NOS_2Cl$: N, 5.18%.

Conversion of the counter anion of the salt XIb into antimony hexachlorate anion by the addition of antimony pentachloride gave *N*-benzoyliminium antimony hexachlorate XIb′: mp 134—135°C; IR (KBr): 1700 cm^{-1} (C=O).

On the other hand, treatment of the reaction mixture with aqueous sodium tetraphenylborate gave only the hydrolyzed product, XVI (X=$B(C_6H_5)_4$: mp 157—158°C;

Found: C, 73.61; H, 6.29; N, 2.80%. Calcd for $C_{28}H_{28}BNS_2$: C, 74.16; H, 6.22; N, 3.09%.

Reaction of Imino-dithiolane IVa with Methacryloyl Chloride. The crystalline adduct was treated with aqueous sodium tetraphenylborate to give XIe in quantitative yield: mp 110°C (recrystallized from acetonitrile);

Found: N, 2.69%. Calcd for $C_{32}H_{32}NOS_2B$: N, 2.65%.

In other cases, the resulting adducts (XIa, c, and d) were difficult to isolate. They were solids stable only in inert solvents.

Acetylation of Aniline with Iminium Salt XI. To the suspension of XIc (prepared from 1.0 g of acetyl chloride and 1.0 g of IVb) in benzene, was added 0.48 g of aniline in benzene. After warming the reaction mixture for one minute on water-bath, the reaction mixture was poured into the cold water to give 0.35 g (52%) of acetanilide: mp 110—112°C (lit., 114°C) (recrystallized from water). The IR spectrum of this product was identical with that of authentic sample of acetanilide.

Reaction of Imino-dithiolane IVa with Alkyl Halides. General Procedure: 2-Methylimino-1,3-dithiolane IVa was mixed with the equimolar amount of alkyl halide in acetonitrile or under neat conditions at room temperature. The iminium salts were isolated as perchlorates by treating with aqueous sodium perchlorate.

Reaction of IVa with Phenacyl Bromide. The imino-dithiolane (11.2 g, 0.084 mol) IVa was mixed with phenacyl bromide (16.8 g, 0.084 mol) in acetonitrile (30 m*l*) at room temperature. Heat evolution took place with the addition of solid sodium perchlorate to the reaction mixture. After about 30 min, the reaction mixture was treated with excess aqueous sodium perchlorate to give the solid, which was washed with water and then with ether: (27 g, 92%); mp 194—195°C, IR (KBr); 1700 cm^{-1} (C=O), 1080 cm^{-1} (ClO_4^-); UV $\lambda_{max}^{H_2O}$ 257.5 mμ.

Found: C, 40.98; H, 4.00; N, 4.02%. Calcd for $C_{12}H_{14}NO_5S_2Cl$: C, 40.98; H. 4.01; N, 3.98%.

Reaction of IVa with Ethyl Bromoacetate. Similarly, IVa (1.3 g, 0.01 mol) was allowed to react with ethyl bromoacetate (1.7 g, 0.01 mol) under neat conditions to give salt (93%). The bromide anion was converted into perchlorate anion by treatment with aqueous sodium perchlorate to give XVb: mp 119.5—120.5°C (recrystallized from ethanol).

Found: C, 29.64; H, 4.31; N, 4.40%. Calcd for $C_8H_{14}NO_6S_2Cl$: C, 30.06; H, 4.41; N, 4.38%.

Reaction of IVa with p*-Nitrobenzyl Bromide.* IVa (6.5 g, 0.03 mol) and *p*-nitrobenzyl bromide (6.5 g, 0.03 mol) in acetonitrile (10 ml) were warmed on a water bath for 1 hr. Cooling the reaction mixture gave the iminium salt XVc containing one mole of water of crystallization. (10.1 g, 92%): mp 84—85°C (recrystallized from acetonitrile).

Found: C, 35.90; H, 4.02; N, 7.62%. Calcd for $C_{11}H_{13}N_2O_2S_2Br\cdot H_2O$: C, 35.98; H, 3.29; N, 7.63%.

Reaction of IVa with Methyl Iodide. A slight excess of methyl iodide was added to a solution of IVa in acetonitrile. Dithiolanium salt XIII was obtained in 90% yield: mp 184—186°C (recrystallized from acetonitrile).

Found: C, 22.08; H, 3.56; N, 5.30%. Calcd for $C_5H_{10}NS_2I$: C, 21.82; H, 3.66; N, 5.09%.

Determination of the pKa of Iminodithiocarbonates. The buffer solution was a mixture of acetic acid (0.35 mol/*l*) and sodium acetate (0.10 mol/*l*). As both IVb and Vb did not completely dissolve in water or in buffer solution, a small amount of ethanol (1—2%) was added to obtain in a clear solution. Concentration of the samples was approximately 1.0—1.7×10^{-4} mol/*l*. The concentrations of sulfuric acid for complete protonation of iminodithiocarbonates were 18.2, 45.5, 57.5, and 57.5 wt % for IVa, IVb, Va, and Vb, respectively. The p*K*a values thus obtained are summarized in Table 3.

TABLE 3. pK_a OF IMINODITHIOCARBONATES

	Wave-length (mμ)	Coefficient			pK_a
		D_{B^-} (H_2O)	D (Buffer soln)	D_{HB} (H_2SO_4)	
IVa	235.0	7400	8200	8300	5.12
	240.0	6600	10100	10500	5.16
	244.5	5800	10700	11200	5.21
	Average				5.16
IVb	237	9800	9400	5700	3.55
	240	9700	9400	5500	3.10
	260	7000	7100	8300	3.14
	265	6400	6700	10200	3.15
	Average				3.24
Va	245	6900	11300	12700	4.71
	250	6100	12100	13500	4.85
	252	5700	12200	13800	4.82
	260	3900	9800	12000	4.61
	Average				4.75
Vb	260	5500	5800	15100	2.75
	265	4700	5000	16100	2.65
	270	4300	4600	14300	2.68
	275	4200	4400	12300	2.61
	Average				2.67