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Tri(hetero)substituted Carbonium Ions. IV. Reactions of *N*,*N*-Dimethyl-*S*,*S'*-dimethyldithiocarbamidium Ion with Various Nucleophiles[*]

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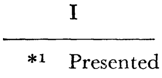
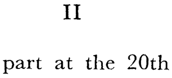
A wide spectrum of electrophilic reactivity has been shown by *N*,*N*-dimethyl-*S*,*S'*-dimethyldithiocarbamidium perchlorate (II). Results obtained reveal that II behaves toward nucleophiles as an ambident electrophile with two reactive sites, a centered electron-definicent carbon and *S*-methyl carbon atom. The electrophilic behavior of II has been compared with that of a cyclic analog, 2-dimethylamino-1,3-dithiolanylium ion, and of a sulfur analog, tris(methylthio)carbonium ion. Attempts to utilize II for synthetic reactions were made. Reactions of II with active methylene compounds gave ketone *N*,*S*-acetals which are of great interest from the standpoint of structural chemistry. *o*-Phenylenediamine and *o*-aminophenol reacted with II to give 2-dimethylamino-benzimidazole and -benzoxazole, respectively, in good yields. The reactions may provide a new method of introducing 2-dialkylamino groups into these heterocycles. Reactions of II with two equivalents of primary amines afforded tetrasubstituted guanidines. Reactions of II with *p*-toluenesulfonylhydrazine and an enamine were also studied.

In our previous papers[1-3] information on the characterization and electrophilic reactivity, of 2-dialkylamino-1,3-dithiolanylium ions (I) was given. The stable carbonium ions behave toward nucleophiles as an ambident electrophile with two reactive sites. *a* and *b* in formula (I) and the reaction course are greatly affected by the nucleophilicity of the reagent used.

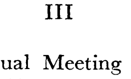
In the present work the electrophilic behavior of an open-chain analog of I, *N*,*N*-dimethyl-*S*,*S'*-dimethyldithiocarbamidium ion (II),[4] has been investigated in detail. Our previous studies on I lead us to expect a similar ambident behavior of II. The reactions of a sulfur analog of II, tris(methylthio)carbonium ion (III) with nucelophiles have been reported.[5]



I



II



III

The purpose of this work is to clarify differences in the electrophilic behavior between open-chain cation II and cyclic I or sulfur analog III, and to utilize II for synthetic reactions.

Results and Discussion

N,*N*-Dimethyl-*S*,*S'*-dimethyldithiocarbamidium perchlorate (IIa) was obtained in 78% yield by methylation of methyl *N*,*N*-dimethyldithiocarbamate with dimethyl sulfate[6] followed by treatment with sodium perchlorate. The white crystals melted at 84—86°C and its NMR spectrum showed two singlet signals at δ 2.85 (SCH_3) and 3.70 ppm (NCH_3).

Reactions with Simple Nucleophiles. In order to demonstrate the spectrum of reactivity of II, the reactions of IIa with a variety of nucleophiles including hydroxide, alkoxides, mercaptides, cyanide and dimethyldithiocarbamate ions were investigated. Scheme 1 indicates products obtained and the possible reaction sequences. Characterization of products isolated includes comparisons of their IR and NMR spectra, boiling and melting points, and refractive indexes with those of authentic compounds.

After our preliminary communication ap-

[*1] Presented in part at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, 1967.

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

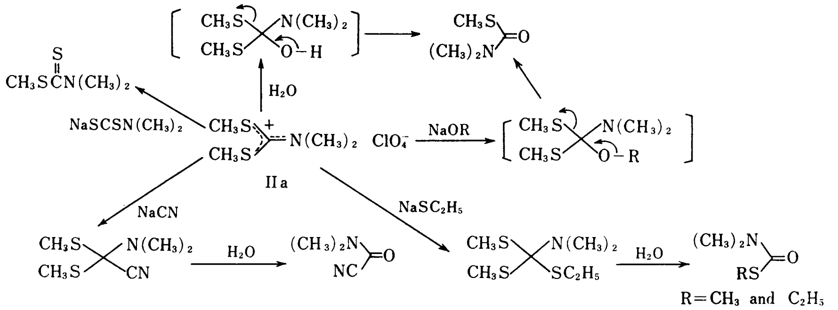
2) T. Nakai and M. Okawara, *Tetrahedron Lett.*, **1967**, 3835; This Bulletin, submitted.

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

4) This cation may be also termed bis(methylthio)-dimethylaminocarbonium ion.[3]

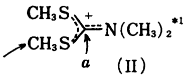
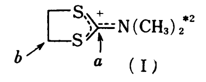
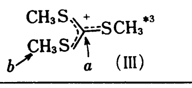
5) W. P. Tucker and G. L. Roof, *Tetrahedron Lett.*, **1967**, 2747,

6) Rinteln and Riester have reported the formation of several methyl sulfate of dithiocarbamidium ions, but no physical properties are available: H. v. Rinteln and O. Riester, *Mitt. Forschungslab. Agfa Leverkussen-München*, **1**, 65 (1955); *Chem. Abst.*, **51**, 7013 (1957).



Scheme 1. Reaction Sequences.

TABLE 1. THE ATTACKING SITE OF NUCLEOPHILES

Nucleophile	 (II)[*1]	 (I)[*2]	 (III)[*3]
$^{-}$OH, $^{-}$OR	*a*	*a*	*a*
$^{-}$CN	*a*	*a*	*a*
$^{-}$SR	*a*	*b*	*a*
$^{-}$SCSNR$_2$	*b*	*b*	*b*[*4]
RNH$_2$	*a*[*5]	*a*	*a*[*4]
R$_3$N	*b*[*6]	[*7]	*b*
R$_2$S	*b*[*6]		

[*1] Unless otherwise indicated, this work.
[*2] Ref. 2.
[*3] Unless otherwise indicated, ref. 5.
[*4] Our unpublished results.
[*5] The results are described below.
[*6] Ref. 7.
[*7] *S*-Vinyl *N*,*N*-dimethyldithiocarbamate was obtained; Ref. 2.

peared,[*1] Tarbell and co-workers briefly reported on reactions of the iodide of II with triethylamine and dimethyl sulfide[7]; II reacts with these nucleophiles to produce the methylated compounds of the nucleophiles and methyl *N*,*N*-dimethyldithiocarbamate. The behavior of II toward nucleophiles are summarized in Table 1 together with those of I and III.

Table 1 shows that, as expected, carbonium ion II is an ambident electrophile with two reactive sites, the centered carbon (*a*) and *S*-methyl carbon atom (*b*) and that, on the whole, II directs the attack of nucleophiles in the same manner as I and III. However, some significant differences between II and I or III were observed; (i) II directs the attack of $^{-}$SEt to position *a*, while I reacts with the anion at position *b*; (ii) under the given conditions II resists reacting with $^{-}SC_6H_4$-CH_3-*p* (see Experimental), but I readily reacts with the anion at position *b*; (iii) II reacts with $^{-}$CN at *a*, while III directs the attack of the anion to *b*; (iv) II directs the attack of NEt$_3$ to *b*, while I reacts with the amine to afford *S*-vinyl dithiocarbamates *via* hydrogen abstraction reactions. Difference (i) is the first example that the reaction course undergoes with a change in the structure of carbonium ion having the same three α-hetero atoms.

These differences cannot be reasonably explained in the present stage. In the case of the reaction with $^{-}$SEt, however, the difference in reaction course between I and II might be interpreted in terms of the stability of the two carbonium ions described below.

According to our classification of reactions, the reaction at site *a* is mode A and the reaction at *b* is mode B, and the former is controlled kinetically and the latter thermodynamically.[2,3] In consequence, the free activation energy for mode A always much less than that for mode B since mode A corresponds to a simple association between the cation and the anion. It might be assumed that the position of equilibrium between the cation and the adduct in mode A should depend upon the difference in free energy (ΔF_A). On the other hand, the fact that II is greatly less stable than I has been confirmed not only by the kinetic observation that the rate of reaction of II with $^{-}$OH is about 10^4 times larger than that of I,[3] but also by the spectral observation that the absorption maximum of II appears at a longer wavelength (276 mμ) than

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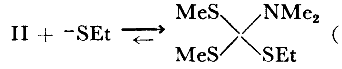
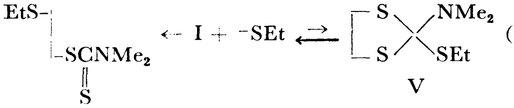
7) J. L. Richard, D. S. Tarbell and E. H. Hoffmeister, *Tetrahedron,* **24**, 6485 (1968).

that of I (249 mμ).[8] It may be further expected that adduct IV from II and $^{-}$SEt is comparable to or slightly less stable than adduct V from I and the anion. Accordingly, it may be said that the difference in free energy between II and IV is larger than that between I and V, *i.e.*, $\Delta F_A(\text{II}) > \Delta F_A(\text{I})$. Alternatively, the position of equilibrium in Eq. 1 is shifted to the right leading to the formation of IV, while the position in Eq. 2 is shifted to the left, which, in turn, results in the formation of β-(ethylthio)ethyl dithiocarbamate (VI) *via* mode B, as found experimentally. These considerations confirm the postulate previously proposed that the major factor deciding the reaction course is the relative position of kinetically controlled product such as IV and V in the energy diagram.

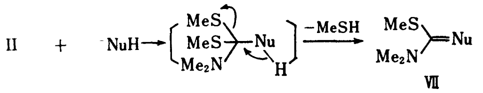

(1)

IV


(2)

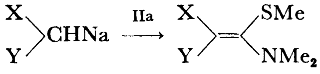
VI V

Furthermore, it is interesting to note that as exemplified in the reaction of II with hydroxide ion, II may be expected to react with nucleophiles bearing an active hydrogen atom ($^{-}$NuH) to afford compounds of a type of ketene *N,S*-acetal (VII), which are of some use from the preparative point of view.

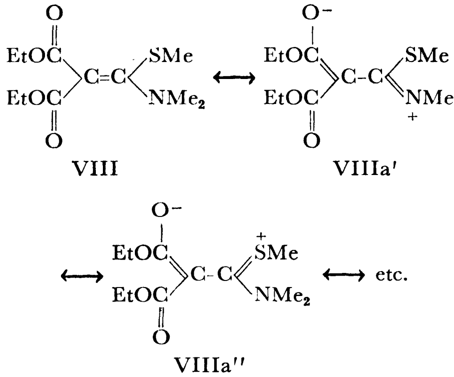

VII

Thus, the reactions of IIa with active methylene compounds, primary amines and an enamine were studied and the results are described below.

Reactions with Active Methylene Compounds. A suspension of IIa and the sodium enolate of active methylene compound in dioxane was stirred at 80°C to afford ketene *N,S*-acetal (VIII) accompanied by evolution of methylmercaptan. These products were identified by IR and NMR spectra. Yields and physical properties of VIII are shown in Table 2.


VIII

These ketene *N,S*-acetals are of special interest from the standpoint of structural chemistry because observations of unusually low barriers to internal rotation around the carbon-carbon double bond may be anticipated.[9] Table 3 shows the


VIII VIIIa′

VIIIa″

Table 2. Yields and physical properties of VIII

Compd.	X	Y	Yield %	Bp/mmHg °C	Mp °C	N, % Found	N, % Calcd
VIIIa	$COOC_2H_5$	$COOC_2H_5$	52	139—141/0.4	—	4.99	5.36
b*1	$COOC_2H_5$	$COCH_3$	28	144—146/0.4	62—65*2	6.10	6.06
c*1	$COOC_2H_5$	CN	68	160—162/0.4	92—93*3	12.95	13.08
d	$COCH_3$	$COCH_3$	41	150—151/0.4	solid*4	6.75	6.96
e	CN	CN	62	—	76—77*3	24.86	25.14

*1 No attempt was made to determine the geometric configration (see text).
*2 Recrystallized from hexane.
*3 Recrystallized from cyclohexane.
*4 Very hygroscopic.

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[8] For the α-hetero atom effects on electronic spectra of tri(hetero)substituted carbonium ions, a definite trend has been observed. As SCH_3 in tris(methylthio)-carbonium ion (III) is progressively replaced by the more electron-donating $N(CH_3)_2$, there is a strong shift of absorption maxima to short wavelengths (high energies). This trend suggests that as the carbonium ion becomes more stabilized, the absorption maximum appears at shorter wavelength. The conclusion has been confirmed by simple Hückel molecular orbital calculations: T. Nakai, K. Hiratani and M. Okawara, unpublished results.

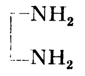
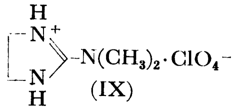
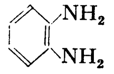
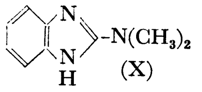
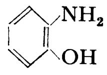
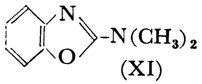
[9] Recently Sandström and co-workers have reported on the observations of low barriers to internal rotation around the C=C bonds in ketene mercaptals and the aminals: G. Isakson, J. Sandström and I. Wennerbeck, *Tetrahedron Lett.*, **1967**, 2233.

Table 3. Spectral data of VIII

Compd.	IR,[*1] cm^{-1}			NMR,[*2] δ ppm		
	$\nu_{C=\overset{+}{N}<}$	$\nu_{C=O}$ ($\nu_{C\equiv N}$)	$\Delta\nu_{C=O}$ ($\Delta\nu_{C\equiv N}$)[*3]	CH_3S	CH_3N	Others
VIIIa	1550	1690	40	2.30 (s)	3.08 (s)	$\underline{CH_3}CH_2$ 1.24 (t)[*4] $CH_3\underline{CH_2}$ 4.07 (q)[*4]
VIIIb	1532	1665 (ester) 1575 (ketone)	80 145	2.40 (s)	3.34 (s)	$\underline{CH_3}CH_2$ 1.24 (t)[*4] $CH_3\underline{CH_2}$ 4.08 (t)[*4] CH_3CO 2.25 (s)
VIIIc	1545	1670 (2210)	70 (∼90)	2.62 (s)	3.25 (s)	$\underline{CH_3}CH_2$ 1.24 (t)[*4] $CH_3\underline{CH_2}$ 4.17 (q)[*4]
VIIId	1525	1575	135			
VIIIe	1545	(2220)				

[*1] Spectra were recorded on KBr disks except for VIIIa (in liquid film).
[*2] Spectra were obtained in CCl_4 (VIIIa, b) and in $CDCl_3$ (VIIIc).
[*3] The difference in wave number between ketene *N,S*-acetal and the parent methylene compound.
[*4] $J=8.0$ Hz.

Table 4. Reactions of IIa with primary amines

Amine	Product	Yield %	Mp °C	C, %		H, %		N, %	
				Calcd	Found	Calcd	Found	Calcd	Found
	 (IX)	56	159—160	28.10	28.10	5.65	5.77	19.67	19.38
	 (X)	90	297—301[*1]	(41.31	41.34	4.62	4.72	16.06	15.91)[*2]
	 (XI)	78	83—85	66.65	66.86	6.22	6.08	17.27	16.79

[*1] Reported mp 301°C: ref. 11.
[*2] For benzimidazolium perchlorate (mp>310°C).

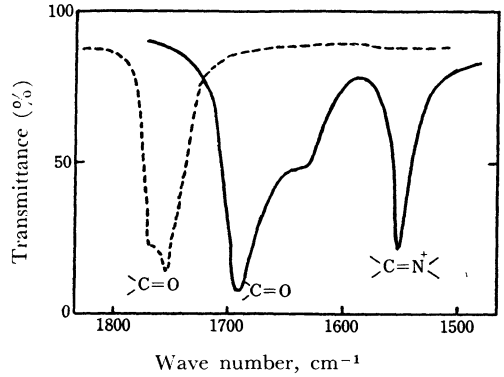
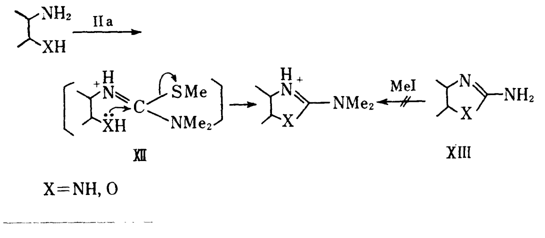


Fig. 1. IR spectra.
——: Diethyl malonate (neat).
- - -: VIIIa (neat).

spectral data of VIII. It is interesting to note that the IR spectra of compounds (VIIIa, b, c and d) showed the carbonyl stretching band ($\nu_{C=O}$) at lower wave numbers than those of the parent methylene compounds. A typical example is shown in Fig. 1. This spectral trend suggests that the polar structures such as VIIIa′ and VIIIa″ significantly contribute to the ground state.

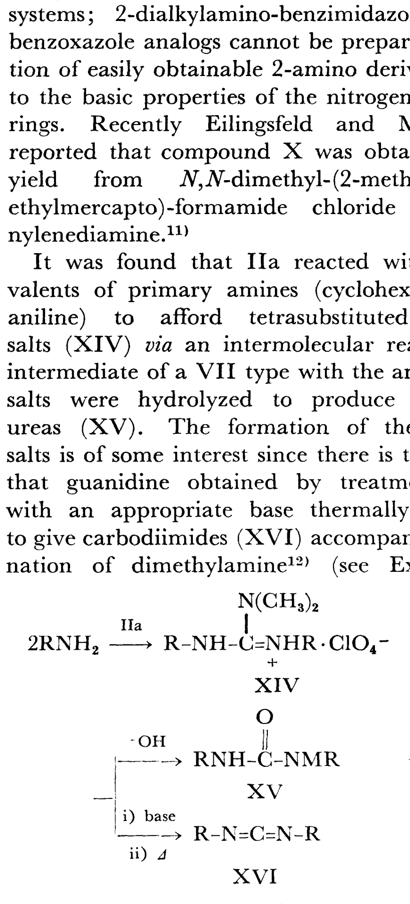
Recently Sandström has reported on unusually low barriers to internal rotation around the C=C bonds in ketene *N,S*-acetals by means of temperature variable NMR spectroscopy.[10] The significant contribution of the polar structures would be responsible for the unusually low barriers to internal rotation. In consequence, it seems to be impossible to determine the geometric configuration of VIIIb and VIIIc at room temperature since a fast interconversion between the *cis* and *trans* isomers occurs.

Reactions with Primary Amines. Carbonium salt IIa reacted with ethylenediamine at 50°C to give an imidazolium salt (IX) in 50% yield. Similarly, carbonium salt IIa reacted with *o*-phenylenediamine and *o*-aminophenol followed by treatment with base to afford 2-dimethylamino-benzimidazole (X) and the benzoxazole derivative (XI), respectively. The formation of these heterocyclic compounds may be explained by the following scheme which involves an intramolecular reaction of intermediate XII of type of VII. Table 4 shows yields and physical properties of these products.



These reactions are of some avail since they provide a new method for introducing dialkylamino groups into the 2 position of these heterocyclic systems; 2-dialkylamino-benzimidazoles and the benzoxazole analogs cannot be prepared by alkylation of easily obtainable 2-amino derivatives owing to the basic properties of the nitrogen atom in the rings. Recently Eilingsfeld and Möbius have reported that compound X was obtained in 57% yield from *N,N*-dimethyl-(2-methoxycarbonyl-ethylmercapto)-formamide chloride and *o*-phenylenediamine.[11]

It was found that IIa reacted with two equivalents of primary amines (cyclohexylamine and aniline) to afford tetrasubstituted guanidium salts (XIV) *via* an intermolecular reaction of the intermediate of a VII type with the amine. These salts were hydrolyzed to produce disubstituted ureas (XV). The formation of the guanidium salts is of some interest since there is the possibility that guanidine obtained by treatment of XIV with an appropriate base thermally decomposes to give carbodiimides (XVI) accompanied by elimination of dimethylamine[12] (see Experimental).



$$2RNH_2 \xrightarrow{IIa} R\text{-}NH\text{-}\overset{N(CH_3)_2}{\underset{+}{C}}{=}NHR\cdot ClO_4^-$$

XIV

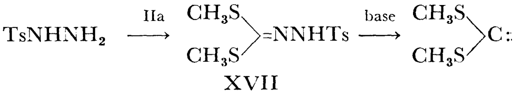
$$\xrightarrow{^-OH} RNH\text{-}\overset{O}{\overset{\|}{C}}\text{-}NMR$$

XV

$$\xrightarrow[ii)\ \Delta]{i)\ base} R\text{-}N{=}C{=}N\text{-}R$$

XVI

In contrast to these primary amines, *p*-toluenesulfonylhydrazine reacted with IIa to give hydrazone XVII accompanied by elimination of dimethylammonium salt. Hydrazone XVII has been employed as a precursor of bis(methylthio)-carbene.[13]



$$TsNHNH_2 \xrightarrow{IIa} \begin{smallmatrix}CH_3S\\CH_3S\end{smallmatrix}\!\!>\!C{=}NNHTs \xrightarrow{base} \begin{smallmatrix}CH_3S\\CH_3S\end{smallmatrix}\!\!>\!C\!:$$

XVII

Reaction with An Enamine. Carbonium salt IIa reacted with 1-*N*-morpholino-1-cyclo-

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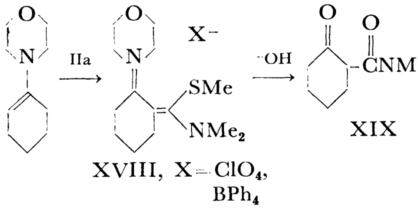
[10] For ketene *N,S*-acetal VIIIc, the following data was available: coalescene temperature (Tc) is −67.5°C and free activation energy for internal rotation (ΔG^*) is 10.4 kcal/mol: J. Sandström, private communication.

[11] E. Eilingsfeld and L. Möbius, *Chem. Ber.*, **98**, 1293 (1965).

[12] W. Weith [*Ber.*, **7**, 1303 (1874)] prepared diphenylcarbodiimide by thermal decomposition of *sym*-triphenylguanidine.

[13] D. M. Lemal and E. H. Banitt, *Tetrahedron Lett.*, **1964**, 245; U. Schöllkopf and E. Wiskott, *Ann.*, **694**, 44 (1966).

hexene to give iminium salt XVIII, a compound of type of VII, which was isolated as tetraphenylborate in 43% yield. Hydrolysis of the salt gave α-(*N*,*N*-dimethylcarbamoyl)cyclohexanone (XIX), which was identified by IR spectrum and by conversion to the 2,4-dinitrophenylhydrazone. The reaction sequences are shown below.



XVIII, X=ClO_4, BPh_4

XIX

Experimental

General. All melting and boiling points are uncorrected. Infrared and ultraviolet spectra were recorded on Hitachi EPI-S2 and EPS-2 spectrometers, respectively. NMR spectra were obtained with a Japan Electron Optics C-60 spectrometer. Chemical shifts are given in parts per million (ppm) from tetramethylsilane as an internal standard. Multiplicity of signals is indicated as follows; s=singlet, t=triplet, q=quartet and m=multiplet.

N,N-Dimethyl-S,S′-dimethyldithiocarbamidium Perchlorate (IIa). Methyl *N*,*N*-dimethyldithiocarbamate (13.5 g, 0.10 mol) was dissolved in 12.5 g (0.10 mol) of dimethyl sulfate. When the mixture was heated to 60°C, a vigorous exothermic reaction occurred. The reaction temperature was kept below 100°C. After the exothermic reaction stopped the mixture was stirred at 90°C for an additional 30 min. The mixture was poured into 100 m*l* of a saturated aqueous solution of sodium perchlorate giving 19.0 g (76%) of pale yellowish precipitate. The precipitate was washed with ether and recrystallized from methanol giving white crystals: mp 84—86°C.

Found: C, 23.73; H, 4.68; N, 5.13%. Calcd for $C_5H_{12}ClNO_4S_2$: C, 24.05; H, 4.85; N, 5.61%.

Hydrolysis of IIa. Carbonium salt IIa (12.5 g, 0.05 mol) was added to a solution of water (1.0 g, 0.05 mol) and triethylamine (5.0 g, 0.05 mol) in 50 m*l* of dioxane. The mixture was stirred at 80°C for 6 hr, then poured into water. The ethereal extract was dried over anhydrous sodium sulfate and the solvent evaporated *in vacuo*. Distillation of the residue gave 3.7 g (62%) of methyl *N*,*N*-dimethylthiolcarbamate; bp 91—92°C/31 mmHg; n_D(21°C) 1.4964 (lit, [14]bp 115—116°C/89 mmHg; n_D(30°C) 1.4932); IR (neat) 1650 cm^{-1} (C=O); NMR (CCl_4): δ 2.26 (s, SCH_3) and 3.00 ppm (s, NCH_3). The infrared spectrum of this distillate was in agreement with that of the authentic sample.

Reactions with Sodium Alkoxides. A suspension of IIa (0.05 mol) and sodium methoxide (8.0 g, 0.15 mol) in 70 m*l* of dioxane was stirred at 70°C for 2 hr. Work-up gave methyl *N*,*N*-dimethylthiolcarbamate in 69% yield.

The reaction of IIa with sodium ethoxide carried out as in the case of sodium methoxide gave the same product in 60% yield.

Reaction with Sodium Cyanide. Carbonium salt IIa (0.05 mol) and sodium cyanide (7.5 g, 0.15 mol) were dissolved in 50 m*l* of dimethylformamide (DMF). The mixture was stirred at 60°C for 5 hr, then poured into an aqueous solution of sodium carbonate. After being put to stand overnight, the mixture was extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate and the solvent evaporated *in vacuo*. Distillation of the residue gave 4.4 g (90%) of *N*,*N*-dimethylcarbamoyl cyanide; bp 39—41°C/1.0 mmHg (lit,[15] 202—203°C); n_D(22°C) 1.4873; IR (neat): 2270 (C≡N) and 1670 cm^{-1} (C=O).

Attempts made to isolate the initial adduct, bis(methylthio)-*N*,*N*-dimethylaminocarbinyl cyanide, failed.

Reaction with Sodium N,N-Dimethyldithiocarbamate. Carbonium salt IIa (0.01 mol) and sodium *N*,*N*-dimethyldithiocarbamate (1.8 g, 0.01 mol) were dissolved in 20 m*l* of DMF. The mixture was stirred at 70°C for 3 hr, then poured into cold water giving 1.1 g (41%) of white precipitate of methyl *N*,*N*-dimethyldithiocarbamate: mp 44—46°C. The IR spectrum of the product was in agreement with that of the authentic sample. The low yield might be due to dissolution of the product in the solvents.

Reactions with Sodium Mercaptides. A suspension of carbonium salt IIa (20.0 g, 0.08 mol) and sodium ethylmercaptide (5.0 g, 0.05 mol) in 50 m*l* of dioxane was stirred at 80°C for 5 hr under a nitrogen atmosphere. The reaction mixture was poured into water, then extracted with ether. The ethereal extract was dried over anhydrous sodium sulfate and the solvent evaporated *in vacuo*. Distillation of the oily residue gave two distillates: bp 55—57°C/51 mmHg (4.7 g) and bp 125—140°C/39 mmHg (1.6 g).

The IR spectrum of the former product showed a strong absorption band at 1650 cm^{-1} (C=O) and the NMR spectrum showed proton signals at δ 2.25 (s, SCH_3), 3.00 (s, NCH_3), 1.25 (t, $\underline{H}_3CH_2S$...

from acetonitrile.

Yields and physical properties of VIII are shown in Tables 2 and 3.

Reaction with Ethylenediamine. Carbonium salt IIa (5.0 g, 0.02 mol) and ethylenediamine (1.2 g, 0.02 mol) were dissolved in 40 m*l* of ethanol. The mixture was refluxed for 5 hr, and the solvent was evaporated *in vacuo* to give precipitates of IX: mp 159—160°C (ethanol).

Reaction with *o*-Phenylenediamine. The reaction of IIa (0.02 mol) and *o*-phenylenediamine (2.0 g, 0.02 mol) carried out as in the case of the reaction with ethylenediamine gave benzimidazolium perchlorate (Xa); mp>310°C (ethanol). Treatment of Xa with an ethanolic solution of sodium methoxide gave 2-dimethylamino-benzimidazole (X).

Reaction with *o*-Aminophenol. The reaction of IIa (0.02 mol) with *o*-aminophenol (2.0 g, 0.02 mol) carried out as in the case of the reaction with *o*-phenylenediamine gave 2-diaethylamino-benzoxazole (XI) (recrystallized from ethanol).

Yields and physical properties of products from reactions with the three amines are shown in Table 4.

Reactions with Primary Amines. *With Cyclohexylamine.* A solution of IIa (0.02 mol) and cyclohexylamine (4.0 g, 0.04 mol) in 50 m*l* of ethanol was heated at 50°C for 5 hr. The solvent was removed *in vacuo* giving a viscous residue. An aqueous solution of $NaBPh_4$ was added to the residue giving a white precipitate of guanidinium salt (XIV; $R=C_6H_{11}$, X=BPh). However, the precipitate did not give satisfactory data of elementary analysis. On the other hand, an aqueous solution of sodium carbonate was added to the viscous residue (XIV, $C=ClO_4$) giving a white precipitate accompanied by evolution of dimethylamine. Recrystallization of the precipitates from ethanol gave colorless needles of *N,N'*-dicyclohexylurea: mp 227—228°C. The IR spectrum of the precipitate was in agreement with that of the authentic sample.

Some attempts were made to prepare carbodiimide from guanidinium salt; a solution of potassium *t*-buthoxide in *t*-buthanol was added to the viscous residue (XIV, $X=ClO_4$) and anhydrous ether was then added to the resulting mixture giving a precipitate of potassium perchlorate. The precipitate was filtered off and the solvents were evaporated from the filtrate giving an oily residue. The residue was heated at 150°C for 2 hr under reduced pressure (30 mmHg). The IR spectrum of the resulting residue showed a strong band at 2200 cm^{-1} presumably due to the –N=C=N– group. However, isolation of dicyclohexylcarbodiimide in pure form was unsuccessful.

With Aniline. The reaction of IIa (0.02 mol) with aniline (3.6 g, 0.04 mol) carried out as in the case of cyclohexylamine gave a viscous residue of guanidinium salt (XIV; R=Ph, $X=ClO_4$). Addition of a solution of $NaBPh_4$ to the residue gave a precipitate of tetraphenylborate: mp 130—132.5°C (from ethanol). However, the data of elementary analysis were unsatisfactory. Treatment of the viscous residue with an aqueous solution of sodium carbonate gave a precipitate of *N,N'*-diphenylurea: mp 233—235°C. The IR spectrum of the precipitate was in agreement with that of the authentic sample.

Reaction with Tosylhydrazine. Tosylhydrazine (3.7 g, 0.02 mol) was suspended in a solution of IIa (0.02 mol) in 40 m*l* of ethanol. The suspension was heated with stirring at 55—60°C for 4 hr. The resulting clear solution was cooled in an ice box giving 2.7 g (61%) of precipitates of XVII. Recrylstallization from ethanol gave colorless needles: mp 149—150°C (lit,[13] 150.5—151.5°C).

Found: C, 41.27; H, 4.92; N, 9.87%. Calcd for $C_{10}H_{14}N_2O_2S_3$: C, 41.38; H, 4.86; N, 9.65%.

Reaction with An Enamine. Carbonium salt IIa (0.02 mol) was added to a solution of 1-*N*-morpholino-1-cyclohexene (0.02 mol) in 30 m*l* of dioxane. The suspension was heated with stirring at 50—60°C for 30 min. The solvent was then evaporated *in vacuo* producing a viscous residue containing iminium salt (XVIII; $X=ClO_4$). An aqueous solution of $NaBPh_4$ was added to the residue giving a precipitate (43%) of iminium salt XVIII ($X=BPh_4$): mp 187—189°C: IR (KBr): 1565 cm^{-1} (C=N).

Found: N, 4.42%. Calcd for $C_{38}N_{45}BN_2OS$: N, 4.76%.

The viscous residue was treated with a dilute aqueous solution of sodium hydroxide and the mixture was extracted with ether. The ethereal layer was dried over anhydrous sodium sulfate. The solvent was then evaporated *in vacuo* affording an oily residue, 2-*N,N*-dimethylcarbamoylcyclohexanone (XIX); IR (neat): 1695 (ketone) and 1645 cm^{-1} (amide). Treatment of the oily residue with 2,4-dinitrophenylhydrazine gave a precipitate of the corresponding hydrazone: mp 83—85°C (ethanol).

Found: C, 51.84; H, 5.30%. Calcd for $C_{13}H_{18}N_5O_5$: C, 51.57; H, 5.48%.

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