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Iminodithiocarbonates. IV. Pyrolyses of *N*-Acyl Immonium Salts of Iminodithiocarbonates

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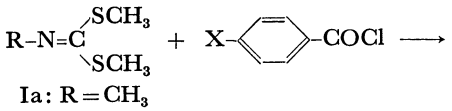
The pyrolyses of *N*-acyl immonium salts of *S,S'*-dimethyl *N*-methyl- (II) and *N*-phenyl-iminodithiocarbonates (III) were studied. *N*-Methyl-immonium salt II gave *S*-methyl *N*-acyl-*N*-methyl-dithiocarbamate (V) at 100°C, but *N*-phenyl derivatives (III) gave phenyl isothiocyanate and *S*-methyl thiolbenzoate (VI) at 140°C. On the other hand, cyclic immonium salt, 2-(*N*-benzoyl-*N*-methyl)-1,3-dithiolanylium chloride (IV) gave 2-benzoylimino-1,3-dithiolane(VII) with elimination of *N*-methyl group at 200°C. It was found that *N*-acyldithiocarbamate V isolated was further decomposed to methyl isothiocyanate and thiolbenzoate at 200°C. Independent syntheses of *N*-acyldithiocarbamates V were performed on the reaction of *N*-monosubstituted dithiocarbamates and acyl chloride.

During the course of our study[1] on the reactivity of *N*-substitued iminodithiocarbonates, we found that the unusually stable *N*-acyl immonium salts were formed on the reaction of iminodithiocarbonates with various acid chlorides at room temperature. In the present paper, studies on the pyrolyses of these *N*-acyl immonium salts (II,III and IV) and the resulting formation of *N*-acyldithiocarbamates (V), isothiocyanates, thiolbenzoate (VI) and 2-benzoylimino-1,3-dithiolane (VII) are reported.

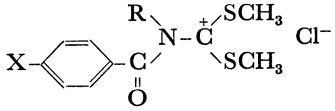
1) Y. Ueno, T. Nakai, and M. Okawara, Submitted, This Bulletin.

Results and Discussion

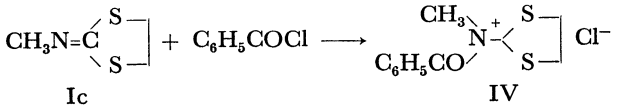
Pyrolysis of N-*Benzoyl Immonium Chloride of* S,S-*Di-*



Ia: R=CH_3
Ib: R=C_6H_5

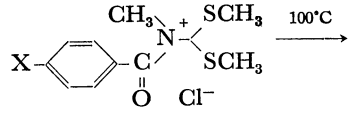


IIa: R=CH_3, X=H
IIb: R=CH_3, X=Cl
IIIa: R=C_6H_5, X=OCH_3
IIIb: R=C_6H_5, X=H

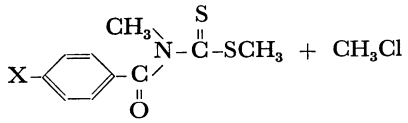


Ic IV

methyl N-*Methyl-Iminodithiocarbonate,II.* Pyrolysis of IIa at 100°C for 9 hr gave methyl *N*-benzoyl-*N*-methyl-dithiocarbamate (Va) in 90% yield. Similarly, the pyrolysis of *N-p*-chlorobenzoyl immonium chloride (IIb) gave methyl *N-p*-chlorobenzoyl-*N*-methyl-dithiocarbamate (Vb) in 79% yield.



IIa: R=H
IIb: R=Cl



Va: R=H
Vb: R=Cl

The structure of V was established by IR, UV and NMR spectra and elemental analysis. The IR spectra showed a band at 1655—1665 cm^{-1} due to the amide-carbonyl group. The UV spectra showed two maximum absorption bands at around 240—260 mμ and 270 mμ which characterized the S-C(=S)- and N-C(=S)- resonance, respectively, in the dithiocarbamate structure. The NMR spectrum of Va fully confirmed the structure (Fig. 1). Thus signals due to S-methyl and *N*-methyl groups appeared as singlets at δ 2.58 and δ 3.66, respectively, and those due to aromatic groups as a multiplet centered at δ 7.50.

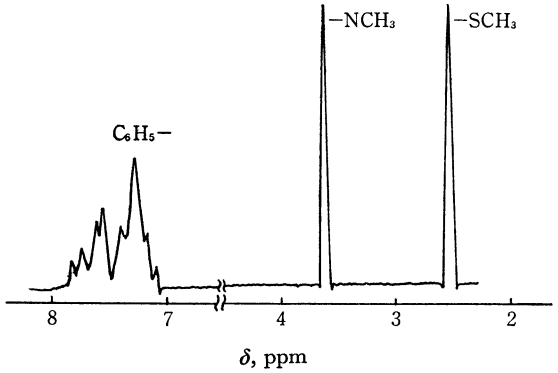
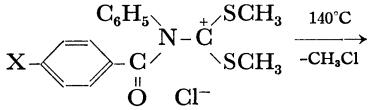
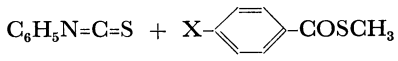


Fig. 1. The NMR spectrum of Methyl *N*-benzoyl-*N*-methyl-dithiocarbamate (Va) in $CDCl_3$.

Pyrolysis of N-*Benzoyl Immonium Chlorides of* S,S'-*Dimethyl* N-*Phenyl-Iminodithiocarbonates, III.* Pyrolysis of IIIa at 140—150°C for 7 hr gave phenyl isothiocyanate and methyl *p*-methoxythiolbenzoate (VIa) in 75 and 65% yield, respectively. Similarly, pyrolysis of the *N*-benzoyl immonium chloride (IIIb) gave phenyl isothiocyanate and methyl thiolbenzoate (VIb). In both cases, at lower temperature such as 100°C decomposition of III did not take place and the *N*-benzoyl dithiocarbamates corresponding to V were not obtained. The structures of phenylis othiocyanate and thiolbenzoate were confirmed by the spectral data and the results of elemental analysis.

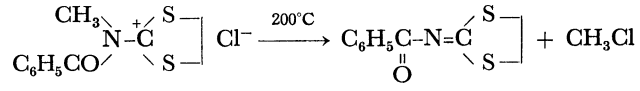


IIIa: X=OCH_3
IIIb: X=H



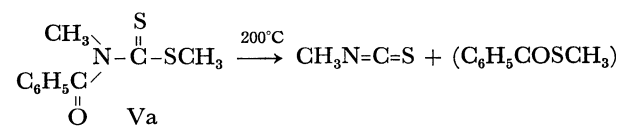
VIa: X=OCH_3
VIb: X=H

Pyrolysis of N-*Benzoyl Immonium Chloride of 2-Methyl-imino-1,3-dithiolane, IV.* Immonium chloride IV was prepared by mixing 2-methylimino-1,3-dithiolane and benzoyl chloride at room temperarture. On being heated, IV melted at about 140°C and then started to decompose at about 190°C. The reaction vessel was kept at 190—200°C for 5.5 hr. The product, 2-benzoylimino-1,3-dithiolane (VII) was obtained in 50% yield. The structure of VII was established by elemental analysis and by comparison of its IR and melting point with the data in literature.[2] The IR spectrum of VII showed a band at 1640 cm^{-1} due to the carbonyl group.



IV VII

Pyrolysis of Methyl N-*Benzoyl*-N-*Methyl-Dithiocarbamate (Va).* Although different types of products were obtained in the pyrolyses of II and III, dithiocarbamate V isolated from II seems to be an intermediate for the formation of isothiocyanate and thiolbenzoate from III. Thus the pyrolysis of *N*-benzoyl dithiocarbamate (Va) was examined. The dithiocarbamate Va was pyrolyzed at 200—220°C for 0.5 hr and resulted in the formation of methyl isothiocyanate in over 54% yield.

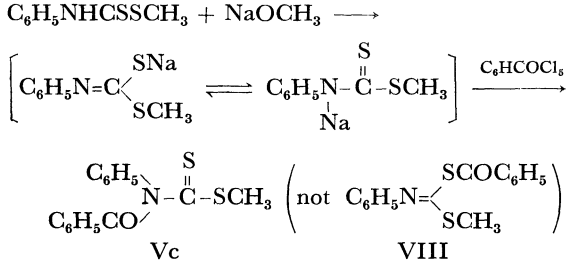


Va

Independent Synthesis of Methyl N-*Benzoyl*-N-*Phenyl-Dithiocarbamate (Vc).* Methyl *N*-benzoyl-*N*-phenyl-dithiocarbamate (Vc) was synthesized by the reaction of methyl *N*-phenyl dithiocarbamate with benzoyl chloride.

2) J. Burkhardt, R. Feinauer, E. Gulbins, and K. Hamann, *Chem. Ber.*, **99**, 1912 (1966).

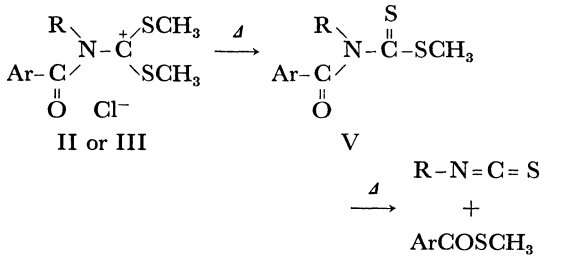
Methyl *N*-phenyl dithiocarbamate was converted into the sodium salt by treating with sodium methoxide in methanol followed by treating with benzoyl chloride in benzene.



The product was assigned as *N*-benzoyl derivative Vc and the isomeric structure of *S*-benzoyl derivative VIII was eliminated by the following facts. (1). The IR spectrum showed a characteristic band of amide-carbonyl group at 1680 cm^{-1} and no band due to the ester carbonyl or imino group. (2). The UV spectrum showed two characteristic absorption at 240 mμ and 270—280 mμ due to S-C(=S)- and -N-C(=S)- resonance, respectively. (3). Formation of no picrate by the addition of picric acid indicates the absence of imino basic group. (4). The product on the reaction of methyl *N*-methyldithiocarbamate with benzoyl chloride was identical in all respects with the methyl *N*-benzoyl-*N*-methyldithiocarbamate (Va).

The structure of phenyl isothiocyanate obtained by pyrolysis of *N*-benzoyldithiocarbamate Vc at 140—150°C was confirmed by its IR spectrum. A new band at 2150 cm^{-1} due to the -N=C=S group in phenyl isothiocyanate appeared.

Pyrolytic Scheme of N-*Acyl Immonium Chloride of Iminodithiocarbonates.* From the result obtained above, the formation of isothiocyanate from *N*-phenylimmonium chloride III can be interpreted by the following scheme involving the intermediacy of the *N*-acyl dithiocarbamate V.



Immonium chloride II or III are pyrolyzed initially to give the dithiocarbamate V with elimination of methyl chloride. Dithiocarbamate V is further decomposed to isothiocyanate and thiolbenzoate. When R is alkyl group, the intermediate dithiocarbamate V was isolated. However, phenyl-substituted dithiocarbamate (Vc) was not isolated and spontaneously decomposed to phenyl isothiocyanate and thiolbenzoate. This indicates the less thermal stability of *N*-phenyl derivative than *N*-alkyl in compound V. While several reactions, RNX-C(=S)Y→RN=C=S+XY, are known for the formation of isothiocyanate with elimination of simple molecule, this is the first example for the formation of isothiocyanate with elimination of thiolbenzoate moiety. In contrast with the open-chain immonium salts (II or III), cyclic immonium salt IV resists the breaking at S–C bond and elimination of *N*-methyl group predominates to produce the 2-benzoylimino-1,3-dithiolane (VII).

Experimental

All melting and boiling points were uncorrected. Infrared and ultraviolet spectra were recorded on a Hitachi infrared EPI-S2 and EPS-2 spectrophotometer, respectively. The NMR spectrum was obtained with a Japan Electron Optics JNL-100 spectrophotometer in a deuteriochloroform solution using tetramethylsilane as an internal standard.

Materials. The immonium chlorides II, III, and IV were prepared by mixing the corresponding iminodithiocarbonates with benzoyl chloride derivatives at room temperature.[1] The acyl immonium chlorides thus obtained were subjected to pyrolyses without isolation.

Pyrolysis of N-*Benzoyl Immonium Chloride of* S,S-*Dimethyl*-N-*Methyl-Iminodithiocarbonate (IIa).* Immonium chloride IIa prepared from Ia (2.7 g, 0.02 mol) and benzoyl chloride (2.8 g, 0.02 mol) were heated at 100°C for 9 hr. By cooling the reaction mixture in a dry ice - acetone bath after the reaction, methyl *N*-benzoyl-*N*-methyl-dithiocarbamate (Va) was obtained (4.0 g, 90%). mp 71.5—72.0°C (recrystallized from *n*-hexane); UV: $\lambda_{max}^{cyclohexane}$ 243.5, 275 mμ, IR: (KBr): $\nu_{C=O}$ 1665 cm^{-1}.

Found: C, 53.73; H, 5.05; N, 6.26%. Calcd for $C_{10}H_{11}NOS_2$: C, 53.33; H, 4.92; N, 6.32%.

Similarly, methyl *N*-*p*-chlorobenzoyl-*N*-methyl-dithiocarbamate Vb was obtained in 79% yield: mp 64.5—65.5°C (recrystallized from *n*-hexane); UV λ_{max}^{EtOH} 260, 276 mμ, IR: $\nu_{C=O}$ 1655 cm^{-1}.

Found: C, 47.05; H, 3.74; N, 4.97%. Calcd for $C_{10}H_{10}NOS_2Cl$: C, 46.25; H, 3.88; N, 5.39%.

Pyrolysis of N-p-*Methoxybenzoyl Immonium Chloride of* S,S'-*Dimethyl*-N-*Phenyl-Iminodithiocarbonate (IIIa).* Immonium chloride IIIa prepared from *N*-phenyl iminodithiocarbonate Ib (4.0 g, 0.02 mol) and *p*-methoxybenzoyl chloride (2.9 g, 0.0017 mol) were heated at 140—150°C for 7 hr. Gas evolution was observed at about 150°C. After decomposition the reaction mixture was subjected to distillation in a vacuum, giving two fractions with a boiling point of 58—69°C/1 mmHg, (1.7 g) and 107—117°C/1 mmHg, (2.0 g). The lower-boiling fraction (74%) was identical in its infrared spectrum (2110 cm^{-1}, N=C=S) and boiling point with those of authentic phenyl isothiocyanate. The higher boiling fraction crystallized after distillation. It was recrystallized from *n*-hexane to give methyl *p*-methoxythiolbenzoate (VIa) with a melting point 41.5—42.0°C (65%); IR (KBr); $\nu_{C=O}$ 1642 cm^{-1}.

Found: C, 59.22; H, 5.30; N, 0.00%. Calcd for $C_9H_{10}O_2S$: C, 59.33; H, 5.53; N, 0.00%.

Similarly, the pyrolysis of *N*-benzoyl immonium chloride IIIb at 140—160°C for 6.5 hr gave a mixture of phenyl isothiocyanate and methyl thiolbenzoate with a boiling point of 56—75°C/4 mmHg. The IR spectrum showed a band at 2110 cm^{-1} (N=C=S) and at 1665 cm^{-1} (C=O). The close boiling point of the two products makes it difficult to separate each component by distillation. The small amount of residue on distillation was recrystallized, and was tentatively assigned as benzanilide by its IR spectrum and melting point (164.5°C). Pyrolysis of IIIb did not take place noticeably at 100°C after 8 hr.

Pyrolysis of N-*Benzoyl Immonium Chloride of 2-Methylimino-1,3-dithiolane, (IV).* 2-Methylimino-1,3-dithiolane (Ic)

(1.33 g, 0.01 mol) was mixed with benzoyl chloride (1.4 g, 0.01 mol) at room temperature. Immonium chloride IV was formed with a slight heat evolution, and which was kept at 190—200°C for 5.5 hr. Cooling the reaction mixture in a dry ice-acetone bath gave 2-benzoylimino-1,3-dithiolane (VII) (1.2 g, 50%): mp 76—77°C (recrystallized from the mixture of ether and petroleum ether) (lit,[2] 79°C): IR (KBr): $\nu_{C=O}$ 1640 cm^{-1} (lit,[2] 1640 cm^{-1}).

Found: C, 53.62; H, 3.78; N, 6.33%. Calcd for $C_{10}H_9NOS_2$: C, 53.78; H, 4.06; N, 6.28%.

Pyrolysis of Methyl N-*Benzoyl*-N-*Methyl-Dithiocarbamate (Va).* Va was heated at 200—220°C for 0.5 hr. Distillation of the reaction mixture gave two fractions with boiling points 70—80°C (0.3 g) and 120°C (0.9 g). Lower boiling fraction was identical in its IR spectrum with an authentic sample of methyl isothiocyanate. Identification of methyl isothiocyanate by transformation into thiourea derivative was carried out using *p*-methoxyaniline in ethanol solution. Recrystallization of the resulting thiourea derivative several times from ethanol gave needles of *N*-methyl-*N*-*p*-methoxyphenyl thiourea: mp 171.0—172.0°C; Found: C, 54.75; H, 5.74; C, 13.99%. Calcd for $C_9H_{12}N_2OS$: C, 55.09; H, 5.17; N, 14.28%.

Higher boiling fraction was assumed to be a mixture of methyl isothiocyanate and methyl thiolbenzoate based on its IR spectrum, at 1670 cm^{-1} (C=O) and 2130, 2240 cm^{-1} (N=C=S), but was not further investigated.

Independent Synthesis of Methyl N-*Benzoyl*-N-*Phenyl-Dithiocarbamate, (Vc).* To a solution of methyl *N*-phenyl-dithiocarbamate (3.7 g, 0.02 mol) in 20 m*l* of methanol, was added sodium methoxide (1.2 g, 0.02 mol). After stirring for 1 hr at room temperature, evaporation of methanol under reduced pressure gave white sodium dithiocarbamate. To a suspension of the sodium dithiocarbamate in 20 m*l* of dry benzene was added benzoyl chloride (2.8 g, 0.02 mol). After refluxing the mixture for 0.5 hr, filtration and evaporation of the solvent gave a yellow solid of methyl *N*-benzoyl-*N*-phenyl-dithiocarbamate (Vc) (2.5 g, 44%): mp 99—100°C (recrystallized twice from *n*-hexane); IR (KBr): $\nu_{C=O}$ 1680 cm^{-1}; UV λ_{max}^{EtOH} 244, 278 mμ.

Found: C, 62.80; H, 4.36; N, 4.90%. Calcd for $C_{15}H_{13}NOS_2$: C, 62.71; H, 4.56; N, 4.88%.

Similarly, methyl *N*-benzoyl-*N*-methyl-dithiocarbamate (Va) was synthesized on the reaction of methyl *N*-methyl-dithiocarbamate and benzoyl chloride. Thus, to a mixture of methyl *N*-methyl-dithiocarbamate (3.0 g, 0.025 mol) and sodium hydroxide (1 g, 0.025 mol) in 12 m*l* of water, was added dropwise benzoyl chloride (3.5 g, 0.025 mol) with stirring and external cooling at 7—10°C. The yellow oil separated was extracted with ether. After drying the etheral solution with anhydrous sodium sulfate, cooling the solution gave crude Va (3.3 g, 59%); mp 68—70°C. The product completely agreed with the pyrolyzed product Va in all respects in the IR and UV spectra.