BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1952—1954 (1967)

Amide Mercaptole. II. The Reactions of *N, N*-Dimethylbenzamide Diethylmercaptole with Some Heavy Metal Compounds

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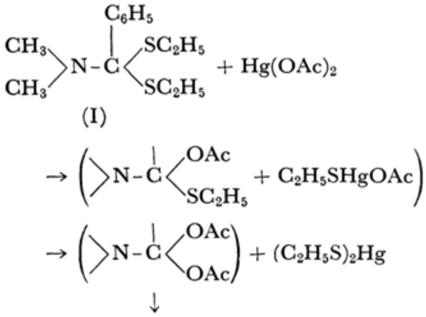
(Received February 22, 1967)

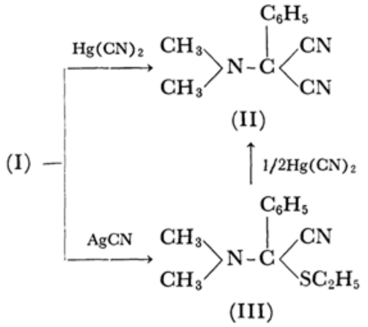
The reactions of *N, N*-dimethylbenzamide diethylmercaptole with mercuric compounds (mercuric oxide, mercuric acetate and mercuric cyanide) or lead(IV) compounds (lead dioxide and lead tetraacetate) have been investigated. Mercuric acetate was found to react easily with the amide mercaptole giving *N, N*-dimethylbenzamide and acetic anhydride with the elimination of mercury ethylmercaptide. In a similar way, mercuric cyanide gave α-dimethylaminophenylmalononitrile in a good yield. Further, it was shown that the amide mercaptole was oxidized by lead dioxide or lead tetraacetate to *N, N*-dimethylbenzamide and diethyl disulfide. The high reactivity of the amide mercaptole toward heavy metal compounds was discussed in comparison with common mercaptals.

It has been shown in the preceding paper[1] that *N, N*-dimethylbenzamide diethylmercaptole (I) reacts with mercuric oxide in acetonitrile to give *N, N*-dimethylbenzamide and mercury ethylmercaptide in good yields. The present paper deals with a further study on the reactions of the amide mercaptole (I) with some heavy metal compounds.

In the first place, mercuric acetate was found to react easily with the amide mercaptole (I) at room temperature in ether giving *N, N*-dimethylbenzamide, acetic anhydride and mercury ethylmercaptide in 75%, 77% and 67% yields, respectively, along with a small amount of mercuric sulfide.



Next, the reaction of the amide mercaptole (I) with mercuric cyanide in tetrahydrofuran at room temperature afforded α-dimethylaminophenylmalononitrile (II) in a 64% yield along with mercury ethylmercaptide. While, α-dimethylamino-α-ethylthiophenylacetonitrile (III) was obtained in a 46% yield when equimolar amounts of silver cyanide and the amide mercaptole (I) were refluxed in tetrahydrofuran for 2 hr. The α-dimethylamino-α-ethylthiophenylacetonitrile (III) did not further react with another one mole of silver cyanide under the same reaction condition; however, it readily reacted with mercuric cyanide at room temperature to give α-dimethylaminophenylmalononitrile (II) and mercury ethylmercaptide.



In view of these results, it is noted that the bonding interaction of mercuric ion toward sulfur atom is stronger than that of silver ion, and so ethylmercapto group of III, deactivated by the introduction of an electron-attracting cyano group, could be eliminated by mercuric cyanide.

Further, it was found that the amide mercaptole (I) was oxidized by such lead (IV) compounds as lead dioxide and lead tetraacetate in benzene, to yield *N, N*-dimethylbenzamide and diethyl disulfide. When the mixture of the amide mercaptole (I) and lead dioxide was heated at 60°C for 6 hr, a yellow precipitate of lead oxide was separated, and *N,N*-dimethylbenzamide and diethyl disulfide were given in 78% and 49% yields, respectively. Similarly, *N, N*-dimethylbenzamide,

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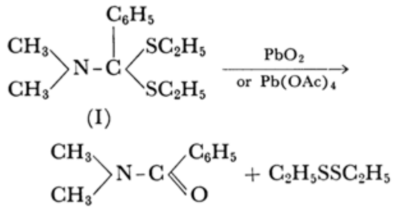
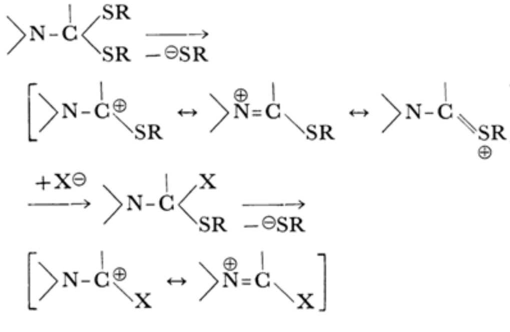
[1] Part I: T. Mukaiyama and T. Yamaguchi, This Bulletin, **39**, 2005 (1966).

diethyl disulfide, acetic anhydride and lead acetate were obtained in good yields by the oxidation with lead tetraacetate.[1]



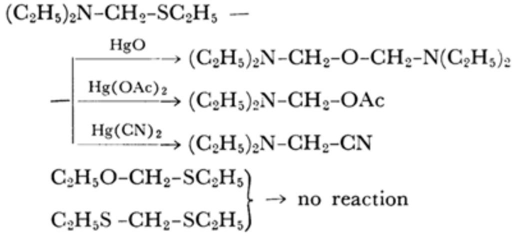
Concerning to the reactions of common mercaptals with heavy metal compounds, Painter has reported that only a single alkylmercapto group was substituted by acetoxy group when mercaptals were treated with mercuric acetate in acetic acid-acetic anhydride.[2] Also, it has been reported that benzaldehyde dibenzylmercaptal reacted with lead tetraacetate to give benzaldehyde diacylal and dibenzyl disulfide in acetic acid but not at all in benzene. This reaction has been considered to be not the direct oxidation of the mercaptal itself, but the oxidation of benzyl mercaptan formed through the exchange reaction between the mercaptal and acetic acid used as a solvent.[3]

The striking difference in behavior between common mercaptals and the amide mercaptole is probably due to a stability of the reaction intermediate, carbonium ion, formed by the elimination of the RS groups. Since nitrogen atom is an excellent electron donor to carbon atom, the carbonium ion adjacent to the nitrogen atom is stabilized as an immonium structure, which facilitates the elimination of the RS groups of amide mercaptole as anions.



Finally, in order to elucidate the effect of substituents, R_2N, RO or RS, upon the elimination of RS group attached to the same carbon atom, the reactions of diethylaminomethyl ethyl sulfide, ethoxymethyl ethyl sulfide and ethylthiomethyl ethyl sulfide (formaldehyde mercaptal) with mercuric compounds were examined. Diethylaminomethyl ethyl sulfide reacted easily with mercuric oxide, mercuric acetate and mercuric cyanide in tetrahydrofuran at room temperature to yield diethylaminomethyl ether, diethylaminomethyl acetate and *N, N*-diethylglycinonitrile, respectively, along with mercury ethylmercaptide. On the other hand, no reaction was observed when ethoxymethyl ethyl sulfide or ethylthiomethyl ethyl sulfide was treated with mercuric cyanide under the same reaction condition and the starting materials were recovered quantitatively.

The conclusion drawn from these experiments is that R_2N group, which is the most excellent electron donor, is most effective for the elimination of RS group as a mercaptide anion.



$$(C_2H_5)_2N\text{-}CH_2\text{-}SC_2H_5 \left\{\begin{array}{l}\xrightarrow{HgO} (C_2H_5)_2N\text{-}CH_2\text{-}O\text{-}CH_2\text{-}N(C_2H_5)_2 \\ \xrightarrow{Hg(OAc)_2} (C_2H_5)_2N\text{-}CH_2\text{-}OAc \\ \xrightarrow{Hg(CN)_2} (C_2H_5)_2N\text{-}CH_2\text{-}CN\end{array}\right.$$

$$\left.\begin{array}{l}C_2H_5O\text{-}CH_2\text{-}SC_2H_5 \\ C_2H_5S\text{-}CH_2\text{-}SC_2H_5\end{array}\right\} \rightarrow \text{no reaction}$$

Experimental[4]

Materials. The preparation of *N, N*-dimethylbenzamide diethylmercaptole (I) has been described in the preceding paper;[1] bp 105—109°C/0.2 mmHg, n_D^{16} 1.5732. Diethylaminomethyl ethyl sulfide,[5] ethoxymethyl ethyl sulfide[6] and ethylthiomethyl ethyl sulfide[7] were synthesized by the methods given in the literatures. Lead tetraacetate was recrystallized from glacial acetic acid and dried over phosphorus pentoxide. Mercuric acetate, mercuric cyanide, silver cyanide and lead dioxide were obtained commercially and used without further purification.

Reaction of the Amide Mercaptole (I) with Mercuric Acetate. To a solution of the amide mercaptole (I) (5.10 g, 0.02 mol) in dry ether (20 m*l*) was added 6.40 g (0.02 mol) of mercuric acetate in portions. Reaction took place immediately with a slight heat evolution. After 15 minutes' stirring, the resulting grayish precipitate was filtered and recrystallized from ethanol to give 2.30 g (67%) of mercury ethylmercaptide; mp 76°C. A small amount (0.35 g) of ethanol insoluble black solid, which may be mercuric sulfide, was obtained as a by-product. The filtrate was concentrated and fractionated to give acetic anhydride (1.57 g, 77%) and *N, N*-dimethylbenzamide (2.25 g, 75%). They were identified by comparing their infrared spectra with those of the authentic samples.

Reaction of the Amide Mercaptole (I) with Silver Cyanide. When a mixture of 2.60 g (0.01 mol) of the amide mercaptole (I) and 1.34 g (0.01 mol) of silver cyanide in dry tetrahydrofuran (25 m*l*) was

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[2] E. P. Painter, *Can. J. Chem.*, **42**, 2018 (1964).

[3] E. J. Bourne, W. M. Corbett, M. Stacey and R. W. Stephenes, *Chem. & Ind. (London)*, **1954**, 106.

[4] All melting points and boiling points are uncorrected.

[5] C. M. McLeod and G. M. Robinson, *J. Chem. Soc.*, **119**, 1474 (1921).

[6] H. Böhme, *Ber.*, **69**, 1613 (1936).

[7] H. Böhme, H. Fischer and R. Frank, *Ann.*, **563**, 67 (1949).

refluxed for 2 hr, a pale yellow silver ethylmercaptide was precipitated. After cooling, the precipitate was filtered off and the filtrate was distilled to yield α-dimethylamino-α-ethylthiophenylacetonitrile (III) (1.00 g, 46%); bp 103—107°C/1.0 mmHg, n_D^{25} 1.5334.

Found: C, 66.26; H, 7.28%. Calcd for $C_{12}H_{16}N_2S$: C, 65.96; H, 7.27%.

Into a solution of 2.24 g (0.01 mol) of III in tetrahydrofuran (20 m*l*) was added 1.26 g (0.005 mol) of mercuric cyanide. Then the mixture was stirred at room temperature for one hour. The resulting white precipitate of mercury ethylmercaptide was filtered off and distillation of the filtrate gave 1.25 g (68%) of α-dimethylaminophenylmalononitrile; bp 121—123°C/12 mmHg, n_D^{25} 1.5078.

Reaction of the Amide Mercaptole (I) with Lead Dioxide. When a mixture of the amide mercaptole (I) (2.00 g, 0.008 mol) and lead dioxide (1.90 g, 0.008 mol) in dry benzene (20 m*l*) was heated at 60°C for 6 hr with stirring, dark-brown color of lead dioxide was disappeared and a yellow precipitate was obtained. The precipitate was filtered off (0.85 g) and distillation of the filtrate gave diethyl disulfide (0.24 g, 49%) and *N, N*-dimethylbenzamide (0.94 g, 78%). Comparison of their infrared spectra with the authentic samples established their identities.

Reactions of Diethylaminomethyl Ethyl Sulfide with Mercuric Compounds. To a solution of diethylaminomethyl ethyl sulfide (3.95 g, 0.02 mol) in dry tetrahydrofuran (20 m*l*) was added 2.16 g (0.01 mol) of mercuric oxide in portions. After a few minutes, reaction set in, and a grayish-white precipitate was separated from the reaction mixture. Stirring was continued for 2 hr at room temperature, and then the precipitate of mercury ethylmercaptide was filtered and recrystallized from ethanol. It weighed 2.90 g (90%). The filtrate was treated with active alumina to remove a trace of mercuric compounds and then the solvent was evaporated *in vacuo*. Distillation of the residue afforded 1.15 g (61%) of diethylaminomethyl ether; bp 66—67°C/26 mmHg, n_D^{25} 1.4409.

Found: C, 63.71; H, 13.13; N, 14.96%. Calcd for $C_{10}H_{24}N_2O$: C, 63.99; H, 12.78; N, 14.80%.

The infrared spectrum of this compound shows an absorption at 1065 cm^{-1}, attributed to a C–O–C bond, and strong absorptions at 2950, 1385 and 1215 cm^{-1}.

Similarly, one mole of mercuric acetate was reacted with two moles of diethylaminomethyl ethyl sulfide in tetrahydrofuran at room temperature to yield diethylaminomethyl acetate (48%); bp 62—65°C/19 mmHg, n_D^{18} 1.4230 (lit.[8] n_D^{18} 1.4226).

Furthermore, by the reaction of diethylaminomethyl ethyl sulfide with mercuric cyanide, *N, N*-diethylglycinonitrile was obtained in a 70% yield; bp 56—60°C/14 mmHg, n_D^{20} 1.4280 (lit.[9] n_D^{25} 1.4230).

Grateful acknowledgment is made to Miss Kazuko Isojima for her microanalyses.

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8) H. Böhme and E. Köhler, *Angew. Chem.*, **72**, 523 (1960).

9) C. F. H. Allen and J. A. VanAllan, "Organic Syntheses," Coll. Vol. III, p. 275 (1955).