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S-Alkylthioamidium Salt. II.[1] The Reactions of S-Alkylthioamidium Iodides with Mercuric Compounds

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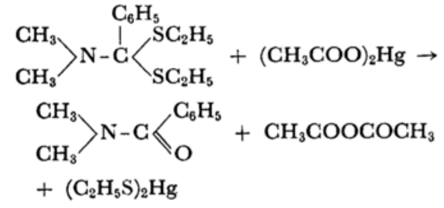
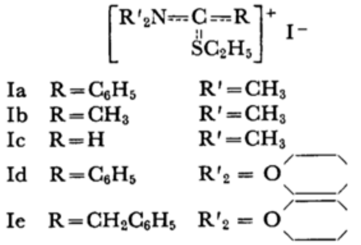
The reactions of S-alkylthioamidium iodides with some mercuric compounds have been studied. Mercuric carboxylates were found to react with S-alkylthioamidium iodides giving the corresponding acid anhydrides and amides in good yields along with alkylmercaptomercuric iodide. In addition, it was established that the reaction of mercuric cyanide with the iodides afforded α-dimethylaminomalononitriles by the elimination of alkylmercapto mercuric iodide. Further, α-morpholino-β-phenylacrylonitrile was obtained in 87% yield by treating S-ethylthiophenylacetomorpholidium iodide with silver cyanide.

In the previous paper, the reaction of *N, N*-dimethylbenzamide diethylmercaptole with mercuric acetate has been reported to yield *N, N*-dimethylbenzamide, acetic anhydride and mercury ethylmercaptide.[2]

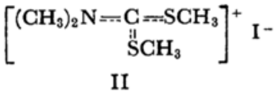


In connection with this reaction, S-ethylthioamidium iodide (I) and its analogs (II and III) were tried to react with mercuric carboxylates in order to find a more convenient method for the preparation of acid anhydride.



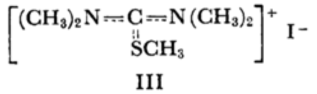
$$\left[\mathrm{R'_2N{=}\underset{\underset{\displaystyle SC_2H_5}{\|}}{C}{=}R}\right]^+ \mathrm{I^-}$$

Ia $R = C_6H_5$ $R' = CH_3$
Ib $R = CH_3$ $R' = CH_3$
Ic $R = H$ $R' = CH_3$
Id $R = C_6H_5$ $R'_2 = O$
Ie $R = CH_2C_6H_5$ $R'_2 = O$



$$\left[\mathrm{(CH_3)_2N{=}\underset{\underset{\displaystyle SCH_3}{\|}}{C}{=}SCH_3}\right]^+ \mathrm{I^-}$$

II



$$\left[\mathrm{(CH_3)_2N{=}\underset{\underset{\displaystyle SCH_3}{\|}}{C}{=}N(CH_3)_2}\right]^+ \mathrm{I^-}$$

III

When mercuric carboxylate was added to a solution of *N, N*-dimethyl-S-ethylthiobenzamidium iodide (Ia) in acetonitrile at room temperature, a yellowish or colorless clear solution was obtained at first with a slight heat evolution, and in a few minutes a white precipitate of ethylmercaptomercuric iodide was separated from the solution. Since the ethylmercapto mercuric iodide (C_2H_5-SHgI), which is 1 : 1 adduct[3] of mercury ethylmercaptide and mercuric iodide, is quite insoluble in almost all solvents, it can be easily separated by filtration. From the filtrate, corresponding acid anhydrides and *N, N*-dimethylbenzamide were obtained in good yields. Mercuric salts of aromatic carboxylic acids were less reactive toward Ia than aliphatic one, and a higher temperature was necessary to obtain the anhydrides in better yields. Lower yield of benzoic anhydride against that of the amide will be due to the hydrolysis of the reactive intermediate by the water of crystallization of mercuric benzoate; indeed, free benzoic acid was also isolated in 19% yield. The results of the reaction of S-alkylthioamidium iodides with some mercuric carboxylates are summarized in Table 1.

The reaction may be considered to proceed as follows. A nucleophilic attack of carboxylate anion upon the central carbon atom of S-alkylthioamidium ion might be assisted by $^+$HgOCOR, which readily abstracts the ethylthio group attached to the same carbon atom;[2] for, by the separate experiment, it was established that sodium carboxylate did not react with S-alkylthioamidium iodide at all under the similar condition. Subsequently, acyloxyimmonium type intermediate would be resulted. The intermediate, in turn,

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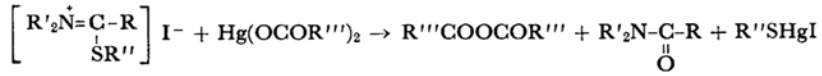
[1] Part I: T. Mukaiyama, T. Yamaguchi and H. Nohira, This Bulletin, **38**, 2107 (1965).

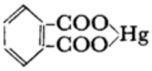
[2] T. Yamaguchi and T. Mukaiyama, *ibid.*, **40**, 1952 (1967).

[3] K. A. Kofmann and W. O. Rabe, *Z. Anorg. Chem.*, **17**, 26 (1898).

TABLE 1. THE REACTION OF *S*-ALKYLTHIOAMIDIUM IODIDES WITH MERCURIC CARBOXYLATES

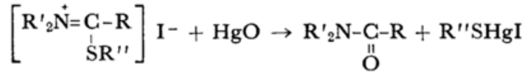


$$\left[\begin{array}{l} R'_2\overset{+}{N}=\underset{|}{C}-R \\ \qquad SR'' \end{array}\right] I^- + Hg(OCOR''')_2 \rightarrow R'''COOCOR''' + R'_2N-\underset{\underset{O}{\|}}{C}-R + R''SHgI$$

S-Alkylthio-amidium iodide	Mercuric carboxylate	Temp. °C	Time hr	Anhydride %	Amide %	R''SHgI %
Ia	$(CH_3COO)_2Hg$	RT	2	85	85.5	93
Ia	$(C_3H_7COO)_2Hg$	RT	2	80	86	96
Id	$(C_3H_7COO)_2Hg$	RT	2	86	82	97
Ia	$((CH_3)_2CHCOO)_2Hg$	RT	4	81	80	94
Ia	$(C_6H_5COO)_2Hg$	RT	4	27	66	—
Ia	$(C_6H_5COO)_2Hg$	50	4	42	88	95
Ia		50	4	53	62	89
II	$(C_3H_7COO)_2Hg$	RT	2	73	72	88
II	$(C_6H_5COO)_2Hg$	RT	2	25	45	75

RT=room temperature

TABLE 2. THE REACTION OF *S*-ALKYLTHIOAMIDIUM IODIDES WITH MERCURIC OXIDE

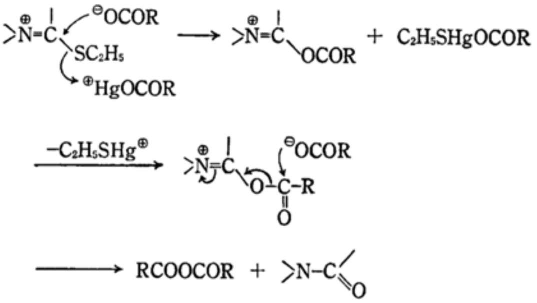


$$\left[\begin{array}{l} R'_2\overset{+}{N}=\underset{|}{C}-R \\ \qquad SR'' \end{array}\right] I^- + HgO \rightarrow R'_2N-\underset{\underset{O}{\|}}{C}-R + R''SHgI$$

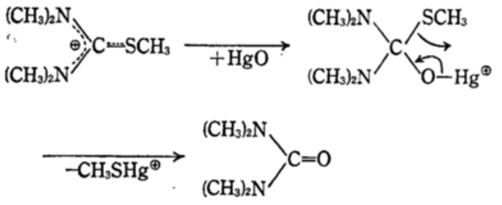
	R	R'_2N	R''	Temp. °C	Time hr	Yield, % R'_2NCOR	Yield, % R''SHgI
Ia	C_6H_5	$(CH_3)_2N$	C_2H_5	RT	5	69	92
Ia	C_6H_5	$(CH_3)_2N$	C_2H_5	80	2	71	84
Id	C_6H_5		CH_3	RT	5	92	94
II	SCH_3	$(CH_3)_2N$	CH_3	RT	7	57	89
III	$N(CH_3)_2$	$(CH_3)_2N$	CH_3	80	5	66	—

RT=room temperature

would act as a strong acylating agent[4] toward another carboxylate anion to form acid anhydride and amide.



Next, the reactions of I, II or III with mercuric oxide were studied. When a suspension of mercuric oxide in acetonitrile was treated with I, II or III, the corresponding *N*, *N*-disubstituted amides, *N*, *N*-dimethyl-*S*-methylthiolcarbamate and *N*, *N*, *N'*, *N'*-tetramethylurea, respectively, were obtained in good yields along with alkylmercaptomercuric iodide (Table 2). It is noted that Id is the most reactive toward mercuric oxide and III is less reactive than I and II. The poor reactivity of III may be due to its high resonance-stabilization of the structure, which retards the nucleophilic attack of mercuric oxide on the central carbon atom.



In addition, it was found that α-dimethylamino-malononitriles (IVa, b, c) were afforded in good yields by treating Ia, Ib or Ic with equimolar

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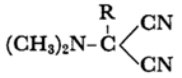
[4] H. K. Hall, *J. Am. Chem. Soc.*, **78**, 2717 (1956).

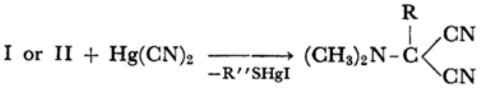
TABLE 3. α-DIMETHYLAMINOMALONONITRILES



$$(CH_3)_2N\text{-}\overset{R}{C}(CN)_2$$

	R	Yield %	Bp °C/mmHg	n_D^{25}		Elemental analyses, % C	H	N
IVa	C_6H_5	92	99/4	1.5102	Found	71.67	6.02	22.50
					Calcd	71.35	5.95	22.70
IVb	CH_3	39	76—77/20	1.4287	Found	58.31	7.02	33.92
					Calcd	58.71	7.37	34.12
IVc	H	63	85/15	1.4331	Found	55.32	6.18	38.65
					Calcd	55.05	6.42	38.53
V	CH_3S	60	102/23	1.4732	Found	46.92	5.89	27.29
					Calcd	46.45	5.81	27.10

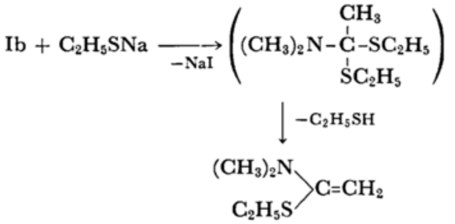
amount of mercuric cyanide in acetonitrile at room temperature. Similarly, II reacted with mercuric cyanide giving α-dimethylamino-α-methylthiomalononitrile (V) in 60% yield. They were identified by elemental analyses and infrared spectra. The results are listed in Table 3.

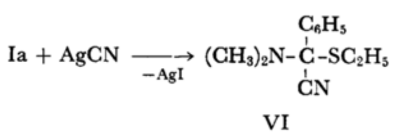


$$\text{I or II} + Hg(CN)_2 \xrightarrow[-R''SHgI]{} (CH_3)_2N\text{-}\overset{R}{C}(CN)_2$$

IVa $R=C_6H_5$
IVb $R=CH_3$
IVc $R=H$
V $R=SCH_3$

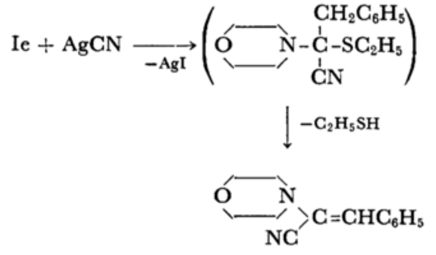
Further, Ia was found to react with silver cyanide in acetonitrile at room temperature giving 61% yield of α-dimethylamino-α-ethylthiophenylacetonitrile (VI) along with silver iodide. On the other hand, when Ie was treated with silver cyanide under the same condition, the evolution of ethyl mercaptan was observed and α-morpholino-β-phenylacrylonitrile (VII) was obtained in 87% yield. The elimination of ethyl mercaptan may be explained by considering the similar pathway, shown in the reaction of Ib with sodium ethylmercaptide giving ketene *N, S*-acetal.[5]





$$\text{Ia} + AgCN \xrightarrow[-AgI]{} (CH_3)_2N\text{-}\underset{CN}{\overset{C_6H_5}{C}}\text{-}SC_2H_5$$

VI



VII

Experimental[6]

Materials. *S*-Alkylthioamidium iodides (Ia—e) were prepared from the corresponding thioamides and alkyl iodides as described previously.[1] Their melting points, yields and analyses are listed in Table 4.

TABLE 4. S-ALKYLTHIOAMIDIUM IODIDES

	Mp °C	Yield %		Elemental analyses, % C	H	N
Ia	130.5—132	92.5	Found	41.36	5.23	4.42
			Calcd	41.12	4.98	4.36
Ib	92—94	94	Found	28.46	5.82	5.99
			Calcd	27.82	5.41	5.41
Ic	107—108	91	Found	24.85	5.09	5.81
			Calcd	24.50	4.93	5.71
Id[11]	152—153	94	Found	41.09	4.76	4.06
			Calcd	41.25	4.58	4.02
Ie	126—127	51	Found	44.35	5.26	3.77
			Calcd	44.56	5.31	3.71

N, N, S, S'-Tetramethyldithiocarbamidium iodide[7] (II) was obtained in 93% yield, when the mixture of the corresponding dithiocarbamate and methyl iodide was

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[5] T. Mukaiyama, S. Aizawa and T. Yamaguchi, This Bulletin, **40**, 2641 (1967).

[6] Melting points and boiling points are uncorrected.

[7] This compound has been reported to melt at 95—96°C by K. Hartke, E. Schmidt, M. Castillo and J. Bartulin, *Chem. Ber.*, **99**, 3268 (1966).

[8] J. Braun and K. Weissback, *Ber.*, **63**, 2846 (1930).

allowed to stand at room temperature for a day long; mp 77—78°C (decomp.).

Found: C, 21.52; H, 4.49; N, 4.83%. Calcd for $C_5H_{12}INS_2$: C, 21.66; H, 4.33; N, 5.05%.

N, N, N', N'-Tetramethyl-*S*-methylthiuronium iodide (III) was synthesized by the reaction of the corresponding thiourea, prepared by the thermal decomposition⁸⁾ of *N, N, N', N'*-tetramethylthiuram disulfide, and methyl iodide in refluxing acetone; mp 172—173°C.

Found: C, 26.59; H, 5.81; N, 10.10%. Calcd for $C_6N_{15}IN_2S$: C, 26.28; H, 5.48; N, 10.21%.

Mercuric salts of isobutyric, *n*-butyric, benzoic and phthalic acid were prepared by the method described in the literature.⁹⁾ Mercuric acetate, mercuric cyanide, mercuric oxide and silver cyanide were obtained from commercial sources.

Reaction of Ia with Mercuric Isobutyrate. To a solution of Ia (6.42 g, 0.02 mol) in acetonitrile (40 m*l*) was added 7.50 g (0.02 mol) of mercuric isobutyrate in portions. Immediately, a clear solution was obtained with a slight heat evolution, and in a few minutes a white precipitate began to separated from the solution. The reaction mixture was then stirred at room temperature for 4 hr. The precipitate of ethylmercaptomercuric iodide (mp 180°C decomp.) was filtered and washed with acetonitrile. It weighed 7.30 g (94%). After the solvent had been evaporated from the filtrate, the residue was distilled under reduced pressure giving 2.56 g (81%) of isobutyric anhydride and 2.39 g (80%) of *N, N*-dimethylbenzamide.

By a similar procedure, the other mercuric carboxylates were converted to the corresponding acid anhydrides by Ia or II. The reaction conditions and results are summarized in Table 1.

Reaction of Id with Mercuric Oxide. Into a stirred suspension of mercuric oxide (2.17 g, 0.01 mol) in 40 m*l* of acetonitrile was added 3.49 g (0.01 mol) of Id in portions. The yellow color of mercuric oxide disappeared gradually. After the stirring had been continued for 5 hr at room temperature, the resulting white precipitate of methylmercaptomercuric iodide (mp 186.5°C decomp.) was filtered and washed with acetonitrile. It weighed 3.51 g (94%). The filtrate was concentrated and distilled under reduced pressure to give 1.75 g (92%) of benzomorpholide; bp 140—141°C/1.5 mmHg, mp 74—75°C (lit.¹⁰⁾ 74°C).

Similarly, *N, N*-dimethyl-*S*-methylthiolcarbamate and *N, N, N', N'*-tetramethylurea were obtained by the reaction of II or III with mercuric oxide (Table 2).

Reaction of Ia with Mercuric Cyanide. To a solution of Ia (16.05 g, 0.05 mol) in acetonitrile (100 m*l*) was added 12.63 g (0.05 mol) of mercuric cyanide. The mixture was stirred at room temperature for 2 hr and the resulting white precipitate of ethylmercaptomercuric iodide was filtered off (18.56 g, 96%). After the acetonitrile had been evaporated from the filtrate, distillation of the residual liquid gave 8.47 g (92%) of α-dimethylaminophenylmalononitrile (IVa); bp 98.5—99.5°C/4 mmHg. The elemental analysis (Table 3) and infrared spectrum of the product were found to be consistent with the structure assigned.

Reaction of Ia with Silver Cyanide. A suspension of Ia (16.05 g, 0.05 mol) and silver cyanide (6.70 g, 0.05 mol) in acetonitrile (100 m*l*) was stirred at room temperature for 2 hr. After the resulting pale yellow precipitate of silver iodide had been filtered off, the filtrate was concentrated and distilled to yield 6.76 g (61%) of α-dimethylamino-β-ethylthiophenylacetonitrile (VI); bp 113°C/1.5 mmHg, n_D^{23} 1.5366. This compound was identified by comparing the infrared spectrum with the authentic sample.²⁾

Reaction of Ie with Silver Cyanide. When a suspension of Ie (3.62 g, 0.01 mol) and silver cyanide (1.29 g, 0.01 mol) in acetonitrile (50 m*l*) was stirred at room temperature, the evolution of ethyl mercaptan was observed and a pale yellow precipitate of silver iodide was separated. After the stirring had been continued for 4 hr, the precipitate was filtered off and the filtrate was concentrated to give a solid, which was then recrystallized from ethanol as colorless needles, mp 100—100.5°C, yield 87%. This compound had the correct analysis for α-morpholino-β-phenylacrylonitrile (VII) and the infrared absorption at 2220 cm⁻¹, assigned for C≡N bond.

Found: C, 72.67; H, 6.28; N, 12.78%. Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.08%.

NMR $\delta_{TMS}^{CDCl_3}$: 2.85 (triplet, 4H, $-N(CH_2-)_2$), 3.65 (triplet, 4H, $O(CH_2-)_2$), 5.92 (singlet, 1H, $-CH=$), 7.15—7.34 (multiplet, 5H, phenyl).

The authors are indebted to Mr. Masaru Koizuka and Miss Kazuko Isojima for elemental analyses.

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9) T. Mukaiyama, H. Nambu and I. Kuwajima, *J. Org. Chem.*, **28**, 917 (1963).

10) R. Fusco and S. Rossi, *Tetrahedron*, **3**, 209 (1958).

11) D. A. Peak and F. Stansfield, *J. Chem. Soc.*, **1952**, 4070.