BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2703—2706 (1968)

Convenient Method for the Preparations of Carboxylic Thiolester and Acid Anhydride

Teruaki MUKAIYAMA and Harumi KATSUYAMA

Laboratory of Organic Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received April 11, 1968)

The reactions of mercuric carboxylates with bivalent sulfur compounds, such as aralkyl sulfides and mercaptoles, were investigated. When mercuric acetate and aralkyl sulfides were refluxed in benzene, mercury mercaptides and aralkyl acetates were obtained. It was made clear that the reactivity of the sulfides depends on the stability of carbonium ions given by elimination of the mercapto group. Next, it was found that acetic anhydride, benzophenone and mercury phenylmercaptide were obtained in high yields by the equimolar reaction of benzophenone diphenylmercaptole with mercuric acetate. Further, the reaction was extended to the preparative method of carboxylic acid anhydrides from free acids by treating the carboxylic acids with diphenylmercury and the mercaptole. On the other hand, *S*-phenyl thioacetate, benzophenone and mercury mercaptide were produced in good yields when benzophenone diphenylmercaptole (2 mol) was treated with mercuric acetate (1 mol). Further, it was established that thiolesters were exclusively produced in good yields along with benzophenone and the mercury mercaptide by the reaction of benzophenone diphenylmercaptole or bis(*p*-chlorophenyl)mercaptole (2 mol) with free carboxylic acids (2 mol) and diphenylmercury (1 mol).

In the preceding paper,[1] it has been shown that acetic anhydride, *N,N*-dimethylbenzamide and mercury ethylmercaptide were obtained in good yields by treating *N,N*-dimethylbenzamide diethylmercaptole with mercuric acetate at room temperature. This reaction was reasoned by considering facile elimination of the mercapto group from *N,N*-dimethylbenzamide diethylmercaptole by an attack of the mercuric acetate yielding a reactive intermediate, acyloxyimmonium ion. In the present experiment, the reactions of phenyl aralkyl sulfides with mercuric acetate were tried first in order to find out the facility of elimination of phenylmercapto group from the sulfides by the attack of the mercuric salt. For example, when phenyl trityl sulfide was treated with mercuric acetate in boiling benzene for 3 hr, mercury phenylmercaptide and trityl acetate were obtained in good yields. It was found that the reaction of phenyl benzhydryl sulfide with mercuric acetate under the same conditions yields only a small amount of benzhydryl acetate and phenylmercapto mercury acetate. But, benzhydryl acetate and mercury phenylmercaptide were obtained in good yields by carrying out the reaction in the presence

TABLE 1. THE REACTION OF PHENYL ARALKYL SULFIDES WITH MERCURIC ACETATE[a)]

Aralkyl group	Catalyst	Yield, %		
		Aralkyl acetate	$(C_6H_5S)_2$-Hg	C_6H_5SHg-$OCOCH_3$
$(C_6H_5)_3C$-	—	70	90	—
$(C_6H_5)_2CH$-	—	33	—	86
$(C_6H_5)_2CH$-	$BF_3\cdot O(C_2H_5)_2$	83	85	—
$C_6H_5CH_2$-	$BF_3\cdot O(C_2H_5)_2$	30	—	

a) These reactions were carried out in refluxing benzene for 3 hr.

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[1] T. Yamaguchi and T. Mukaiyama, This Bulletin, **40**, 1952 (1967).

of a catalytic amount of boron trifluoride etherate (see Table 1).

$$C_6H_5SR + \tfrac{1}{2}(CH_3CO_2)_2Hg \rightarrow CH_3CO_2R + \tfrac{1}{2}(C_6H_5S)_2Hg$$

R: Aralkyl

These results show that the reactivity of the aralkyl sulfides decreases in the following sequence: $(C_6H_5)_3C\text{-} > (C_6H_5)_2CH\text{-} > C_6H_5CH_2\text{-}$. This order also suggests that the ease of carbon-sulfur bond fission[2] is dependent on the stability of carbonium ions formed by elimination of the mercapto group.

Next, the reactions of the mercaptoles with mercuric carboxylates were tried with the assumption that acid anhydrides, the ketone and mercury mercaptide would be produced as in the case of the reaction of mercuric acetate with *N,N*-dimethylbenzamide diethylmercaptole.

Concerning the reactions of mercaptals with heavy metal salts, Painter reported[3] that one of the ethylmercapto group of penta-*O*-acetyl diethylmercaptals of some hexoses was substituted by an acetoxy group when the mercaptals were treated with mercuric acetate. Bourne also reported[4] that the reaction of benzaldehyde dibenzylmercaptal with lead tetraacetate gave benzylidene diacetate, dibenzyl disulfide and lead acetate.

It was established that acetic anhydride, benzophenone and mercury phenylmercaptide were obtained in good yields by treating benzophenone diphenylmercaptole with mercuric acetate in boiling benzene in the presence of a catalytic amount of boron trifluoride etherate, as expected. Benzophenone diphenylmercaptole was chosen as the mercaptole with the expectation that it would readily eliminate the mercapto group, activated by two phenyl and a phenylmercapto groups attached to the same carbon.

$$(C_6H_5)_2C(SC_6H_5)_2 + (CH_3CO_2)_2Hg \rightarrow (CH_3CO)_2O + (C_6H_5)_2CO + (C_6H_5S)_2Hg$$

68% 96% 96%

Next, the reactions of carboxylic acids, diphenylmercury and the mercaptole were tried to explore a convenient method for the synthesis of acid anhydrides starting from free acids with the consideration that the mercuric carboxylates would be produced from free acids and diphenylmercury. Indeed, various acid anhydrides, benzophenone and mercury phenylmercaptide were obtained in good yields by refluxing 2 mol of free carboxylic acids, 1 mol of diphenylmercury and 1 mol of the mercaptole in anhydrous benzene for a few hours in the presence of a catalytic amount of boron trifluoride etherate. The results are listed in Table 2.

$$(C_6H_5)_2C(SC_6H_5)_2 + 2RCO_2H + (C_6H_5)_2Hg \xrightarrow{-2C_6H_6} (RCO)_2O + (C_6H_5)_2CO + (C_6H_5S)_2Hg$$

TABLE 2. THE REACTIONS OF BENZOPHENONE DIPHENYLMERCAPTOLE (1 MOL) WITH FREE CARBOXYLIC ACIDS (2 MOL) AND DIPHENYLMERCURY (1 MOL)[a)]

Carboxylic acid	Yield, %		
	Acid anhydride	Benzophenone	$(C_6H_5S)_2Hg$
Acetic	67	94	85
Propionic	55	88	94
n-Butyric	63	94	80
Cinnamic	74	75	80
Benzoic[b)]	51	90	87

a) These reactions were carried out in refluxing benzene for 4 hr in the presence of a catalytic amount of boron trifluoride etherate.

b) In the case of benzoic acid, 11% yield of *S*-phenyl thiobenzoate based on benzoic acid was also obtained.

On the other hand, it was found that *S*-phenyl thioacetate, benzophenone and mercury phenylmercaptide were produced in high yields by treating 2 mol of benzophenone diphenylmercaptole with 1 mol of mercuric acetate under the same conditions.

$$2(C_6H_5)_2C(SC_6H_5)_2 + (CH_3CO_2)_2Hg \rightarrow 2CH_3COSC_6H_5 + 2(C_6H_5)_2CO + (C_6H_5S)_2Hg$$

63% 92% 97%

The use of diphenylmercury extended this reaction to a preparative method of thiolesters starting from free carboxylic acids on the basis of the similar consideration as mentioned above. The reactions of benzophenone diphenylmercaptole or bis(*p*-chlorophenyl)mercaptole (2 mol) with free carboxylic acids (2 mol) and diphenylmercury (1 mol) in boiling benzene in the presence of a catalytic amount of boron trifluoride etherate gave *S*-phenyl or *S*-*p*-chlorophenyl thiocarboxylates, benzophenone and the mercury mercaptide in high yields. The results are listed in Tables 3 and 4.

$$2(C_6H_5)_2C(SC_6H_4\text{-}X\text{-}p)_2 + 2RCO_2H + (C_6H_5)_2Hg \xrightarrow[-2C_6H_6]{} 2RCOSC_6H_4\text{-}X\text{-}p + 2(C_6H_5)_2CO + (p\text{-}X\text{-}C_6H_4S)_2Hg$$

X: H or Cl

The formation of acid anhydrides or thiolesters can be explained by considering an initial formation of an intermediate (1) from mercuric carboxylates

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[2] D. S. Tarbell and D. P. Harnish, *J. Am. Chem. Soc.*, **74**, 1862 (1952).

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

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

TABLE 3. THE REACTIONS OF BENZOPHENONE DIPHENYLMERCAPTOLE (2 MOL) WITH FREE CARBOXYLIC ACIDS (2 MOL) AND DIPHENYLMERCURY (1 MOL)[a)]

Carboxylic acid	Yield, %		
	S-Phenyl thiocarboxylate	Benzophenone	$(C_6H_5S)_2$-Hg
Acetic	94	94	98
Propionic	84	96	97
n-Butyric	68	93	98
Benzoic	79	84	98
o-Chlorobenzoic	81	96	98
p-Toluic	79	94	95
p-Anisic	76	84	96
p-Nitrobenzoic[b)]	—	36	72
Cinnamic	77	98	98

a) These reactions were carried out in refluxing benzene for 5 hr in the presence of a catalytic amount of boron trifluoride etherate.

b) In the case of *p*-nitrobenzoic acid, only 37% yield of *p*-nitrobenzoic anhydride resulted.

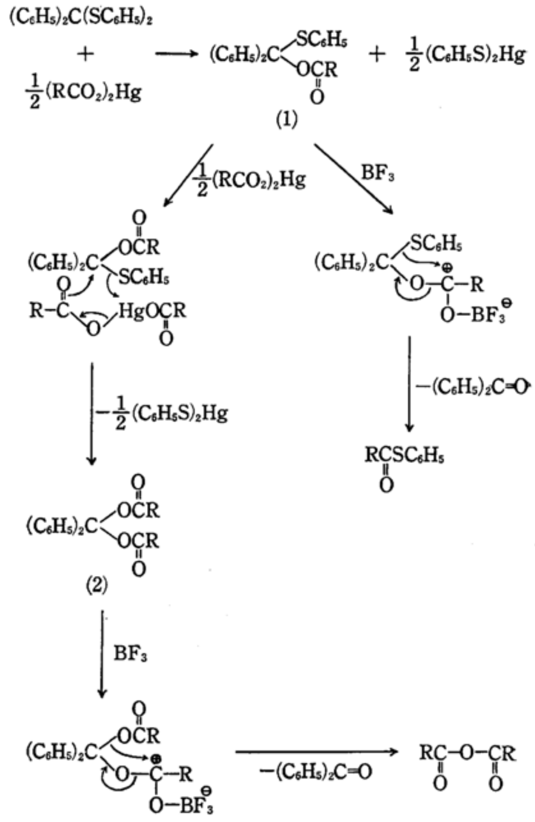
TABLE 4. THE REACTIONS OF BENZOPHENONE BIS(*p*-CHLOROPHENYL)MERCAPTOLE (2 MOL) WITH FREE CARBOXYLIC ACIDS (2 MOL) AND DIPHENYLMERCURY (1 MOL)[a)]

Carboxylic acid	Yield, %		
	S-*p*-Chlorophenyl thiocarboxylate	Benzophenone	$(C_6H_5S)_2$-Hg
Acetic	84	88	98
n-Butyric	75	98	98
n-Stearic	60	73	92
Benzoic[b)]	21	44	98
p-Anisic	79	93	98
Cinnamic	88	96	98

a) These reactions were carried out in refluxing benzene for 2 hr in the presence of a catalytic amount of boron trifluoride etherate.

b) In the case of benzoic acid, 34% yield of benzoic anhydride based on benzoic acid was obtained together with the thiolester.

and the mercaptole. When one half mole of mercuric carboxylates are used, thiolesters are exclusively produced from the intermediate (1) by an intramolecular nucleophilic displacement. On the other hand, in the presence of an additional half mole of mercuric carboxylates, the intermediate (1) further reacts with them to give the second intermediate (2), an acylal, by a nucleophilic attack of the mercapto group on the mercury atom. The second intermediate (2) then yields benzophenone and acid anhydrides by the aid of boron trifluoride.



Experimental

Reaction of Phenyl Trityl Sulfide with Mercuric Acetate. A solution of phenyl trityl sulfide (3.52 g, 0.01 mol) and mercuric acetate (1.59 g, 0.005 mol) in 20 m*l* of anhydrous benzene was refluxed for 3 hr. After cooling the reaction mixture, the precipitate was filtered off to give mercury phenylmercaptide, 1.76 g (82%), mp 150°C. The filtrate was evaporated *in vacuo*. The addition of 10 m*l* of anhydrous ether-petroleum ether mixture (1 : 1 v/v) to this residue gave the precipitate containing the mercury salt, and the sulfide was recovered. It was filtered off and the filtrate was concentrated under reduced pressure. To the resulted oil a small amount of anhydrous petroleum ether was added and this mixture was heated until it became a homogeneous solution. Trityl acetate was obtained as colorless crystals from the solution, 2.10 g (70%), mp 83°C (Found: C, 82.81; H, 6.06%).

Reaction of Phenyl Benzhydryl Sulfide with Mercuric Acetate in the Presence of a Catalytic Amount of Boron Trifluoride Etherate. A solution of phenyl benzhydryl sulfide (2.76 g, 0.01 mol) and mercuric acetate (1.59 g, 0.005 mol) in 20 m*l* of benzene was refluxed for 3 hr in the presence of a catalytic amount of boron trifluoride etherate. After cooling the reaction mixture, the precipitate of mercury phenylmercaptide (1.76 g, 85%) was filtered off and the filtrate was evaporated *in vacuo*. The residue was distilled to give benzhydryl acetate, 1.95 g (86%), bp 124°C/1 mmHg (Found: C, 79.40; H, 5.96%).

Equimolar Reaction of Benzophenone Diphenylmercaptole with Mercuric Acetate. A solution of benzophenone diphenylmercaptole (7.64 g, 0.02 mol) and mercuric acetate (6.36 g, 0.02 mol) in 40 m*l* of anhydrous benzene was refluxed for 0.5 hr in the presence of a catalytic amount of boron trifluoride etherate. After cooling the reaction mixture, the precipitate was filtered off to give mercury phenylmercaptide, 8.10 g (97%). The filtrate was concentrated and distilled to give 1.39 g (68%) of acetic anhydride, bp 70—72°C/90 mmHg, and 3.32 g (92%) of benzophenone.

Reaction of Benzophenone Diphenylmercaptole (1 mol) with Cinnamic Acid (2 mol) and Diphenylmercury (1 mol). A solution of benzophenone diphenylmercaptole (3.82 g, 0.01 mol), cinnamic acid (2.96 g, 0.02 mol) and diphenylmercury (3.54 g, 0.01 mol) in 40 m*l* of anhydrous benzene was refluxed for 4 hr in the presence of a catalytic amount of boron trifluoride etherate. After the reaction mixture was cooled, the precipitate was filtered off to give mercury phenylmercaptide, 3.33 g (80%), and the filtrate was evaporated *in vacuo*. The addition of 10 m*l* of alcohol to this residue gave the precipitate of cinnamic anhydride, 2.05 g (74%), mp 136°C (Found: C, 77.92; H, 5.10%). The filtrate was evaporated *in vacuo* and the residue was distilled to give benzophenone, 1.39 g (75%) and a small amount of cinnamic acid recovered.

Reaction of Benzophenone Diphenylmercaptole (2 mol) with Mercuric Acetate (1 mol). A solution of benzophenone diphenylmercaptole (3.82 g, 0.01 mol) and mercuric acetate (1.59 g, 0.005 mol) in 20 m*l* of anhydrous benzene was refluxed for 0.5 hr in the presence of a catalytic amount of boron trifluoride etherate. After the reaction mixture was cooled, the precipitate was filtered off to give mercury phenylmercaptide, 1.92 g (92%). The filtrate was evaporated *in vacuo* and the residue was distilled to give *S*-phenyl thioacetate, 0.96 g (63%), bp 63°C/0.3 mmHg and benzophenone, 1.69 g (92%) (Found: C, 62.85; H, 5.58%).

Reaction of Benzophenone Bis(*p*-chlorophenyl)mercaptole (2 mol) with Acetic Acid (2 mol) and Diphenylmercury (1 mol). A solution of benzophenone bis(*p*-chlorophenyl)mercaptole (3.82 g, 0.01 mol), acetic acid (0.60 g, 0.01 mol) and diphenylmercury (1.77 g, 0.005 mol) in 20 m*l* of anhydrous benzene was refluxed for 2 hr in the presence of a catalytic amount of boron trifluoride etherate. After the reaction mixture was cooled, the precipitate was filtered off to give mercury *p*-chlorophenylmercaptide, 2.07 g (98%). The filtrate was evaporated *in vacuo* and the residue was distilled to give *S*-*p*-chlorophenyl thioacetate, 0.78 g (84%), bp 142—144°C/20 mmHg, and benzophenone, 1.60 g (88%).

Found: C, 51.71; H, 3.78%. Calcd for C_8H_7OClS: C, 51.49; H, 3.78%.

Reaction of Benzophenone Diphenylmercaptole (2 mol) with *p*-Toluic Acid (2 mol) and Diphenylmercury (1 mol). A solution of benzophenone diphenylmercaptole (3.84 g, 0.01 mol), *p*-toluic acid (1.36 g, 0.01 mol) and diphenylmercury (1.77 g, 0.005 mol) in 20 m*l* of anhydrous benzene was refluxed for 5 hr in the presence of a catalytic amount of boron trifluoride etherate. After the reaction mixture was cooled, the precipitate was filtered off to give mercury phenylmercaptide, 1.98 g (95%). The filtrate was evaporated *in vacuo* and the crystalline residue was washed with 2 portions of 10 m*l* of anhydrous pentane. The crystalline product was *S*-phenyl *p*-thiotoluate, 1.80 g (79%), mp 91.5—92°C (from alcohol).

Found: C, 73.38; H, 5.31%. Calcd for $C_{14}H_{12}OS$: C, 73.67; H, 5.30%.

The pentane solution was evaporated *in vacuo* and the resulting oil was distilled to give benzophenone, 1.71 g (94%).

The authors wish to express their hearty thanks to Mr. Khoichi Wada for his help during this experiment. Grateful acknowledgment is also made to Miss Kazuko Isojima for her microanalyses.