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A Convenient Method for the Preparation of Acid Anhydrides from Metallic Carboxylates

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A convenient method for the preparation of carboxylic anhydrides by use of one mole of *N,N'*-dicyclohexylthiourea and two moles of silver or mercurous carboxylate has been established. According to this method, several carboxylic anhydrides were obtained in high yields under mild conditions even by microscale experiments.

In previous papers,[1,2] it has been reported that carboxylic anhydrides were prepared from the corresponding mercuric carboxylates by treatment with the addition compound of dibenzoylethylene and triphenylphosphine, or by treatments with *S*-ethylthioamidium iodide.

In the present study, a general preparative method of acid anhydrides was investigated with the expectation that acid anhydride would be formed by the reaction of *N,N'*-dicyclohexylthiourea with silver carboxylates through an intermediate, imidoyl acylate. Indeed, when one mole of *N,N'*-dicyclohexylthiourea was added to a suspension of two moles of finely pulverized silver benzoate in anhydrous acetone at room temperature, benzoic anhydride was obtained in 93% yield along with *N,N'*-dicyclohexylurea and silver sulfide.

$$2\,RCOOAg + C_6H_{11}NHCSNHC_6H_{11} \xrightarrow{\text{Room temp.}} (RCO)_2O + C_6H_{11}NHCONHC_6H_{11} + Ag_2S$$

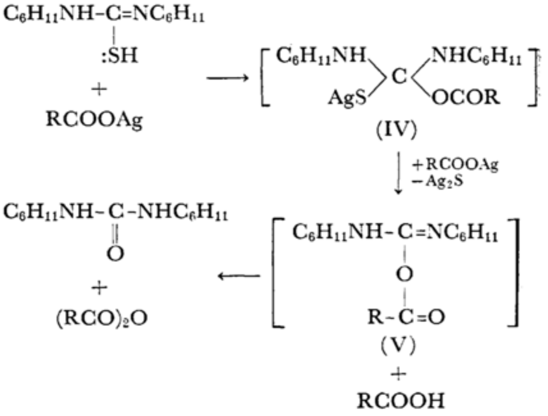
$$R:\ C_6H_5$$

In a similar manner, acetic, propionic, phthalic and succinic anhydrides were obtained from the corresponding silver carboxylates. These data are recorded in Table 1.

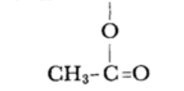
TABLE 1. ACID ANHYDRIDES FROM SILVER CARBOXYLATES

Silver salt (0.04 mol)	Yield of acid anhydride, %	Solvent	m*l*
Acetate	68.0	Acetone	13
Propionate	88.4	Acetone	20
Benzoate	93.0	Acetone	10
Phthalate	86.9	Acetonitrile	30
Succinate	90.0	Chloroform	30

The reaction is considered to proceed through an intermediate (IV), produced from a silver carboxylate and *N,N'*-dicyclohexylthiourea. The IV in turn reacts with another silver carboxylate to form silver sulfide and the imidoyl acylate (V), which further reacts with carboxylic acid to give an acid anhydride and *N,N'*-dicyclohexylurea.

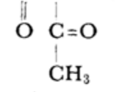


In addition, it was found that mercuric acetate also reacts with *N,N'*-dicyclohexylthiourea to give acetic anhydride, *N,N'*-dicyclohexylurea and mercuric sulfide along with a considerable amount of *N*-acetyl-*N,N'*-dicyclohexylurea (VI), a rearrangement product of imidoyl acylate (Va).



$C_6H_{11}NH-C(=NC_6H_{11})-O-C(=O)-CH_3$

(Va)



$C_6H_{11}NH-C(=O)-N(C_6H_{11})-C(=O)-CH_3$

(VI)

Some mercuric carboxylate, such as mercuric benzoate, contains one mole of water of crystallization, which cannot be removed by the ordinary procedure. Since water reacts with imidoyl benzoate faster than with carboxylate ion, mercuric carboxylates containing water of crystallization cannot be used in this reaction. Next, since anhydrous mercurous carboxylates are easily prepared from sodium carboxylates and mercurous nitrate,

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[1] I. Kuwajima and T. Mukaiyama, *J. Org. Chem.*, **29**, 1385 (1964).

[2] T. Yamaguchi, K. Inomata and T. Mukaiyama, This Bulletin, **41**, 673 (1968).

the reactions of the carboxylates with *N,N'*-dicyclohexylthiourea were tried in order to avoid the above-mentioned trouble. When two moles of mercurous benzoate were allowed to react with one mole of *N,N'*-dicyclohexylthiourea, benzoic anhydride was obtained in a quantitative yield along with mercuric sulfide, metallic mercury and *N,N'*-dicyclohexylurea.

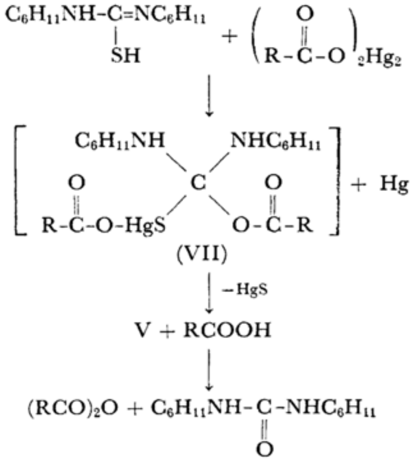
$$(RCOO)_2Hg_2 + C_6H_{11}NHCSNHC_6H_{11} \xrightarrow{\text{Room temp.}}$$
$$(RCO)_2O + C_6H_{11}NHCONHC_6H_{11} + HgS + Hg$$
$$R:\ C_6H_5$$

Similarly, acetic, propionic, phthalic and succinic anhydrides were obtained in high yields from the corresponding mercurous carboxylates. The results are listed in Table 2.

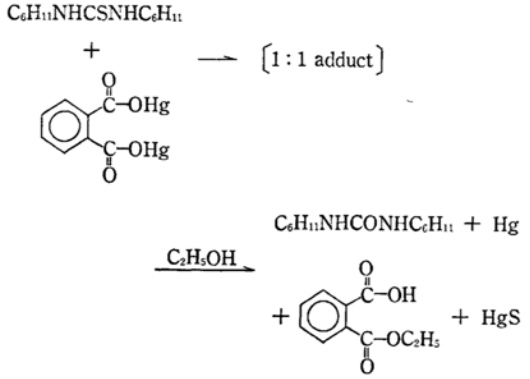
TABLE 2. ACID ANHYDRIDES FROM MERCUROUS CARBOXYLATES

Mercurous salt (0.04 mol)	Yield of acid anhydride, %	Solvent	m*l*
Acetate	69.0	Acetone	15
Propionate	99.2	Acetone	10
Benzoate	98.0	Acetone	30
Phthalate	81.1	Acetonitrile	25
Succinate	95.0	Chloroform	40

The reaction proceeds through an intermediate (VII), which loses mercuric sulfide to form the imidoyl acylate (V), a compound similar to that described in the case of silver carboxylate.



Further, it was found that one of the intermediates (IV), an 1 : 1 adduct, was successfully isolated in a quantiative yield as greenish white precipitates by treating mercurous phthalate (1 mmol) with *N,N'*-dicyclohexylthiourea (1 mmol) in a mixed solvent of anhydrous benzene (4 m*l*) and petroleum ether (1 m*l*). The adduct instantly reacted with ethanol at room temperature to give monoethyl ester of phthalic acid along with *N,N'*-dicyclohexylurea, metallic mercury and mercuric sulfide.



In conclusion, it is noted that mercurous carboxylates react with *N,N'*-dicyclohexylthiourea more easily than mercuric carboxylates and, in each reaction, the yield of acid anhydride markedly depend on the nature and the amount of solvent used as shown in Tables 1 and 2, probably due to the solubility of the intermediate complex (IV).

Experimental

Materials. *N,N'*-Dicyclohexylthiourea,3) silver carboxylates4) and mercurous carboxylates5) were prepared by known procedures. They were ground and dried over P_2O_5 in vacuum desiccator before use.

The Preparation of Propionic Anhydride by the Reaction of *N,N'*-Dicyclohexylthiourea and Silver Propionate. *N,N'*-Dicyclohexylthiourea (4.8 g, 0.02 mol) was added to a suspension of silver propionate (7.24 g, 0.04 mol) in 20 m*l* of dry acetone and was continuously stirred about 15 hr at room temperature. During 2 hr, the suspension changed gradually from white to black. Then the black precipitates were filtered and washed with dry acetone. The filtrate and the washings were combined and evaporated. Propionic anhydride, 2.30 g (88.4%), bp 165—169°C, was obtained by distillation. After distillation, remaining oil solidified at room temperature. Recrystallization from benzene - petroleum ether gave *N*-propionyl-*N,N* -dicyclohexylurea, (0.6 g, 10.7%), mp 127—129°C. The black precipitate was throughly washed with ethanol. After evaporation of ethanol, *N,N'*-dicyclohexylurea, 4.17 g (93%), mp 218°C, was obtained.

Similarly, acetic, benzoic, succinic and phthalic anhydrides were obtained from the corresponding silver or mercurous carboxylates. The reaction conditions and the yields are summarized in Tables 1 and 2. According to this preparative method, except in the cases of acetic and propionic anhydrides, practically pure carboxylic anhydrides were separated by simply removing the black precipitate.

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3) A. Skita and H. Rolfes, *Ber.*, **53**, 1247 (1920).
4) R. A. Zingaro, *J. Am. Chem. Soc.*, **71**, 575 (1949).
5) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart (1954).