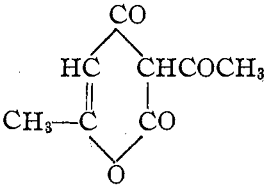

. To accomplish this, 3-carboxy-γ-lutidone, the compound obtained by the rearrangement of dehydro-acetic acid with sulfuric acid and then by treatment with ammonia, was synthesized by a method which left no doubt as to its structure.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

CERTAIN REACTIONS OF THE ALKYL AND ARYL MERCURIC HYDROXIDES

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Although alkyl mercuric hydroxides have been known since 1853,[2] the properties of these compounds have never been extensively studied. Early investigators report these substances as strong bases,[3] but recently Maynard and Howard[4] have shown them to be very weak bases. The aryl mercuric hydroxides[5] have also been prepared but a study of their properties has also been neglected. Beyond the reaction of the alkyl and aryl mercuric hydroxides with acids to give salts, very little is known concerning them. This research had as its purpose, a study of certain chemical reactions of both alkyl and aryl mercuric hydroxides. A comparison of their reactivity with that of mercuric oxide has been made.

The method most commonly used for the preparation of alkyl and aryl mercuric hydroxides has previously been by the action of silver oxide on alkyl or aryl mercuric halides. A much simpler procedure has been used in this research, namely, the reaction of sodium hydroxide in absolute alcohol upon an absolute alcoholic solution of an alkyl or aryl mercuric chloride.[6] The sodium chloride is filtered off and the hydroxides are ob-

[1] This communication is an abstract of a thesis submitted by I. A. Koten in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Frankland, *Ann.*, **85**, 363 (1853). Cahours, *J. prakt. Chem.*, [2] **8**, 397 (1873). *Jahresber.* **1873**, 517; *Compt. rend.*, **76**, 1403 (1874). Eichler, *Ber.*, **12**, 1880 (1879). Seidel, *J. prakt. Chem.*, [2] **29**, 135 (1884). Tiffeneau, *Bull. sci. pharmacol.*, **28**, 65 (1921). Sneed and Maynard, THIS JOURNAL, **44**, 2946 (1922).

[3] Dünhaupt, *Ann.*, **92**, 381 (1854).

[4] Maynard and Howard, *J. Chem. Soc.*, **123**, 960 (1923).

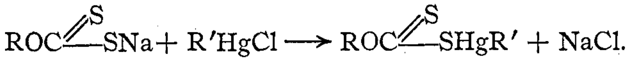
[5] Otto, *J. prakt. Chem.*, [2] **1**, 183 (1870). Dimroth, *Ber.*, **35**, 2043 (1902). Reissert, *Ber.*, **40**, 4209 (1907). Fränkel, "Arzneimittel-Synthese" Julius Springer, **1921**, 5th ed., pp. 677–680.

[6] Mills and Adams, THIS JOURNAL, **45**, 1842 (1923).

tained by evaporation of the alcohol or by evaporation of part of the alcohol and precipitation with ether. In most of the reactions studied, however, the alcoholic solution of the alkyl or aryl mercuric hydroxide was used directly without isolation of the compound.

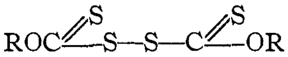
Alkyl and aryl mercuric hydroxides react like sodium hydroxide with an alcohol and carbon disulfide yielding alkyl or aryl mercuric alkyl xanthates of the general formula $\mathrm{ROC}\overset{\mathrm{S}}{\diagup\!\!\diagup}\!\!-\mathrm{SHgR'}$ where R′ is aliphatic or aromatic: $\mathrm{ROH} + \mathrm{CS_2} + \mathrm{R'HgOH} \longrightarrow \mathrm{ROC}\overset{\mathrm{S}}{\diagup\!\!\diagup}\!\!-\mathrm{SHgR'} + \mathrm{H_2O}$.

The structure was proved conclusively by preparing the same substances from an alkyl or aryl mercuric chloride and sodium xanthate.



$$\mathrm{ROC}\overset{\mathrm{S}}{\diagup\!\!\diagup}\!\!-\mathrm{SNa} + \mathrm{R'HgCl} \longrightarrow \mathrm{ROC}\overset{\mathrm{S}}{\diagup\!\!\diagup}\!\!-\mathrm{SHgR'} + \mathrm{NaCl}.$$

The compounds are white and well crystallized. They gradually decompose on long standing or rapidly decompose in sunlight. They react with iodine in chloroform solution to give alkyl or aryl mercuric iodides and yellow oils which are very probably compounds of the formula



$$\mathrm{ROC}\overset{\mathrm{S}}{\diagup\!\!\diagup}\!\!-\mathrm{S{-}S{-}C}\overset{\mathrm{S}}{\diagup\!\!\diagup}\!\!-\mathrm{OR}$$

The reaction of the alkyl or aryl mercuric hydroxides with carbon disulfide and alcohols to form xanthates apparently takes place smoothly and quantitatively, provided only that traces of sodium hydroxide are present. When the mercuric hydroxides were made by the action of silver oxide upon the corresponding mercuric iodides and were then treated with carbon disulfide in alcohol, the reaction products were not the pure xanthate but a mixture of the xanthate and a second substance which proved to be the alkyl or aryl mercuric mercaptan. The addition of a small amount of sodium hydroxide, however, prevented entirely the formation of the mercaptan. That the by-products just mentioned were mercaptans was shown by their synthesis from the alkyl or aryl mercuric hydroxides and hydrogen sulfide.

When the alkyl or aryl mercuric hydroxides were allowed to react with carbon disulfide alone without the presence of alcohol, the mercaptans were formed quantitatively in every case. The presence of a trace of alkali did not interfere with this reaction.

$$\mathrm{RHgOH} + \mathrm{CS_2} \longrightarrow \mathrm{RHgSH} + \mathrm{COS}$$

The preparation of the carbonates of the alkyl and aryl mercuric hydroxides has not always been attended with perfect success. Dünhaupt[7] reports the formation of ethyl mercuric carbonate and states that it crystallized with difficulty. Maynard and Howard,[4] on the other hand,

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[7] Dünhaupt, *J. prakt. Chem.*, **61**, 432 (1854).

were unable to isolate an alkyl mercuric carbonate from carbon dioxide and alkyl mercuric hydroxides. Otto[5] reports the formation of phenylmercuric carbonate by the action of carbon dioxide upon the corresponding hydroxide. In this investigation no precipitate was obtained when carbon dioxide was bubbled through an alcoholic solution of the alkyl mercuric hydroxides. When, however, the alcoholic solution was evaporated at room temperature with carbon dioxide bubbling through the solution continuously, a crystalline product was obtained after all of the alcohol had been removed. This substance was dissolved in dry pyridine, the solution saturated with carbon dioxide and dry ether added. There were thus produced white crystalline products which, upon analysis, proved to be bicarbonates. On the other hand, carbon dioxide passed into an alcoholic solution of aryl mercuric hydroxides gave precipitates of the normal carbonates which separated first as gels but after continuous passage of carbon dioxide for some time became crystalline.

The alkyl mercuric bicarbonates and the aromatic carbonates react with carbon disulfide and alcohol in a manner similar to the hydroxides, undoubtedly due to the fact that hydrolysis takes place very readily.

In a recent paper, Kharasch[8] reported an interesting reaction of the mercuric salt of trinitrobenzoic acid. When this was heated above its melting point, two molecules of carbon dioxide were lost and 2,2′, 4,4′,6,6′-hexanitro-mercury-diphenyl was produced. The alkyl or aryl mercuric salts of trinitrobenzoic acid undergo a similar reaction when heated above the melting point, with the formation of alkyl-aryl or aryl-aryl mercury compounds. $[(NO_2)_3C_6H_2COO]_2Hg \longrightarrow 2CO_2 + [(NO_2)_3C_6H_2]_2Hg$; $(NO_2)_3C_6H_2COOHgR' \longrightarrow CO_2 + (NO_2)_3C_6H_2HgR'$.

It was hoped that it might be possible to use the alkyl or possibly aryl mercuric hydroxides in a manner similar to mercuric oxide for the introduction of an alkyl or aryl mercury group into various types of organic compounds. It was found, however, that the alkyl and aryl mercuric hydroxides did not react with malonic ester, aceto-acetic ester, cinnamic ester, or a phenol under the conditions used for the reactions with mercuric oxide.

Experimental Part

Alkyl Mercuric Halides.—For the preparation of the alkyl mercuric halides, the dialkyl mercury compounds[9] were treated in a hot alcoholic solution with one molecular equivalent of alcoholic mercuric chloride or iodide.

Alkyl Mercuric Hydroxides.—An alcoholic solution of an alkyl mercuric chloride was treated with an absolute alcoholic solution of one molecular equivalent of sodium hydroxide. The sodium chloride was precipitated, filtered off and the filtrate evaporated to dryness at room temperature, or evaporated to a small volume and treated with dry ether.

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[8] Kharasch, This Journal, **43**, 2238 (1921).

[9] Marvel and Gould, *ibid.*, **44**, 153 (1922).

Alkyl and Aryl Mercuric Alkyl Xanthates: General Procedure.—To the alcoholic solution of the alkyl or aryl mercuric hydroxide obtained from one mole of the corresponding mercuric chloride and one mole of sodium hydroxide, in 200 cc. of absolute alcohol, was added 15 cc. of carbon disulfide. A faint yellow color developed, accompanied by a slight rise in temperature. Upon partial evaporation of the solution by means of a current of air, at room temperature, the alkyl or aryl mercuric alkyl xanthates precipitated. After recrystallization from 95% alcohol, white crystalline products were obtained.

The yields of these compounds averaged 70% of those calculated.

The alkyl or aryl mercuric alkyl xanthates are soluble in ether, chloroform and hot alcohol and insoluble in water. Exposed to sunlight, they rapidly turn black.

When treated with a chloroform solution of iodine until no more iodine was absorbed, the alkyl or aryl mercuric alkyl xanthates gave the corresponding alkyl or aryl mercury iodides and a yellow oil.

Table I

Alkyl and Aryl Mercuric Alkyl Xanthates

		Analyses				
					Hg	
	M. p. °C.	Subs. G.	$AgNO_3$ Cc.	NaCN Cc.	Calc. %	Found %
Methyl mercuric methyl xanthate, $CH_3O—CS—SHgCH_3$	59	0.2344	8.80 0.0250 *N*	19.90 0.0478 *N*	62.23	62.46
Methyl mercuric ethyl xanthate, $C_2H_5O—CS—SHgCH_3$	69	0.2633	7.95 0.0250 *N*	20.90 0.0470 *N*	59.56	59.43
Ethyl mercuric ethyl xanthate, $C_2H_5O—CS—SHgC_2H_5$	53	0.2424	3.05 0.1159 *N*	20.05 0.0258 *N*	57.19	57.10
n-Propyl mercuric ethyl xanthate, $C_2H_5O—CS—SHgC_3H_7(n)$	38–39	0.2186	5.38 0.0260 *N*	14.97 0.0490 *N*	55.07	55.35
n-Butyl mercuric ethyl xanthate, $C_2H_5O—CS—SHgC_4H_9(n)$	Oil	....	.....	....	...	...
				NH_4SCN Cc.		
p-Tolyl mercuric ethyl xanthate, $C_2H_5O—CS—SHgC_6H_4CH_3(p)$	128	0.1400	.....	6.55 0.1044 *N*	48.57	48.50
				KSCN Cc.		
p-Tolyl mercuric methyl xanthate, $CH_3O—CS—SHgC_6H_4CH_3(p)$	145	0.1542	.....	10.70 0.07238 *N*	50.35	50.38
				NH_4SCN Cc.		
Benzyl mercuric ethyl xanthate, $C_2H_5O—CS—SHgCH_2C_6H_5$	74	0.2001	.....	9.34 0.1034 *N*	48.59	48.41

Methylmercuric Mercaptan, CH_3HgSH.—When 5 g. of methylmercuric bicarbonate was added to 15 cc. of carbon disulfide, a precipitate formed. This was recrystallized from alcohol and then gave silvery plates melting at 143°.

The same substance was produced by passing hydrogen sulfide into an alcoholic solution of methylmercuric hydroxide.

Upon exposure to sunlight, the substance turned black within two minutes.

Anal. Subs., 0.1617: 24.75 cc. of KSCN (0.0523 *N*). Calc. for CH_4HgS: Hg, 80.74. Found: 80.64.

Ethylmercuric Mercaptan, C_2H_5HgSH.—This substance was formed in exactly the same way as the methylmercuric mercaptan. It was crystallized from absolute alcohol, giving silvery plates melting at 104°.

Anal. Subs., 0.1532, 0.2100: 22.20, 30.60 cc. of KSCN (0.0523 *N*). Calc. for C_2H_6HgS: Hg, 76.71. Found: 76.08, 76.38.

p-Tolylmercuric Mercaptan, p-$CH_3C_6H_4HgSH$.—When 2 g. of *p*-tolylmercuric carbonate was added to 20 cc. of carbon disulfide, a clear solution resulted accompanied by the evolution of carbon dioxide. In a short time a yellow product separated which was insoluble in all the ordinary solvents. The same compound was also produced by the action of carbon disulfide upon *p*-tolylmercuric hydroxide.

Methylmercuric Bicarbonate, CH_3HgHCO_3.—A solution of pure methylmercuric hydroxide was made in absolute methyl alcohol. The solution was evaporated by a current of air while carbon dioxide was passed through continuously. The solid residue which was produced was then dissolved in cold dry pyridine, the solution saturated with carbon dioxide and an excess of dry ether added. The white granular precipitate melted at 123°.

Anal. Subs., 0.1568, 0.1525: 15.45, 15.10 cc. of KSCN (0.0730 *N*). Calc. for $C_2H_4O_3Hg$: Hg, 72.56. Found: 72.28, 72.33.

p-Tolylmercuric Carbonate, $(CH_3C_6H_4Hg)_2CO_3$.—A solution of *p*-tolylmercuric hydroxide in absolute ethyl alcohol was treated with carbon dioxide. A gelatinous mass formed which gradually became crystalline. The compound was insoluble in the ordinary solvents except acetic acid which decomposed it. It decomposes above 260°.

Anal. Subs., 0.1539, 0.1464: 9.00, 8.57 cc. of NH_4SCN (0.1044 *N*). Calc. for $C_{15}H_{14}O_3Hg_2$: Hg, 62.37. Found: 61.26, 61.28.

Ethylmercuric-2,4,6-trinitrobenzoate, $(NO_2)_3C_6H_2COOHgC_2H_5$.—An alcoholic solution of ethylmercuric hydroxide prepared from sodium hydroxide and ethylmercuric chloride was added to an alcoholic solution of 1 molecular proportion of 2,4,6-trinitrobenzoic acid. A precipitate soon formed which was purified by recrystallization from absolute alcohol. It formed white plates melting at 164°.

Anal. Subs., 0.2179, 0.2018: 12.2, 11.35 cc. of NH_4SCN (0.0724 *N*). Calc. for $C_9H_7O_8N_3Hg$: Hg, 41.36. Found: 40.97, 40.92.

Ethylmercuric-2,4,6-trinitrophenyl, $(NO_2)_3C_6H_2HgC_2H_5$.—In a small flask immersed in an oil-bath at 165°, 7 g. of ethylmercuric-2,4,6-trinitrobenzoate was heated until effervescence ceased. The red-brown residue was recrystallized from 70% alcohol forming slightly yellow needles; m. p., 86°.

Anal. Subs., 0.1618, 0.1548: 25.05, 25.05 cc. of HCl (0.0714 *N*); 9.50, 9.75 cc. of NaOH (0.0714 *N*). Calc. for $C_9H_7O_8N_3Hg$: N, 9.50. Found: 9.36, 9.62.

p-Tolylmercuric-2,4,6-trinitrobenzoate, $(NO_2)_3C_6H_2COOHgC_6H_4CH_3(p)$.—This compound was made in a manner similar to the ethylmercuric-2,4,6-trinitrobenzoate. It was insoluble in the common solvents and melted at 227°.

Anal. Subs., 0.2010, 0.1981: 25.05, 25.05 cc. of HCl (0.0714 *N*); 15.00, 14.94 cc. of NaOH (0.0714 *N*). Calc. for $C_{14}H_9O_8N_3Hg$: N, 7.66. Found: 7.56, 7.64.

***p*-Tolylmercuric-2,4,6-trinitrophenyl,** $(NO_2)_3C_6H_2HgC_6H_4CH_3(p)$.—Ten g. of *p*-tolyl mercuric-2,4,6-trinitrobenzoate was heated in a small flask immersed in an oil-bath at 220–230° until effervescence ceased. The brown product obtained was extracted with hot acetone which dissolved a portion of the substance. Upon evaporation of the acetone filtrate, a yellow compound was obtained which, after recrystallization from a mixture of acetone and alcohol, was pale yellow and melted at 192°.

Anal. Subs., 0.2055: 25.05 cc. of HCl (0.0714 *N*); 7.75 cc. of NaOH (0.0714 *N*). Calc. for $C_{13}H_9O_6N_3Hg$: N, 8.33. Found: 8.43.

Method of Analysis.—A method similar to that of Rupp[10] was found to be very satisfactory for analysis of these mercury compounds.

According to his procedure, a 0.2g. sample of the mercury compound is first decomposed by 10 cc. of 7% fuming sulfuric acid and 5 cc. of fuming nitric acid. The addition of 10 cc. of water in small portions generated sufficient heat to effect decomposition. A solution of potassium permanganate was then added until its color persisted for five minutes. The excess of permanganate was removed by a ferrous sulfate solution. Two cc. of 10% ferric alum indicator and 50 cc. of water were then added to the clear solution and the mercury was titrated by means of standard potassium or ammonium thiocyanate until a faint pink tinge appeared.

Summary

1. The alkyl and aryl mercuric hydroxides react with carbon disulfide and alcohol to give alkyl mercuric xanthates of the type  $\mathrm{RO}\overset{\diagup\!\!\!\diagup S}{\mathrm{C}}\mathrm{-SHgR'}$, thus showing a similarity to the alkali hydroxides. Sodium hydroxide acts as a catalyst in the formation of the alkyl mercuric xanthates.

2. The alkyl and aryl mercuric hydroxides and carbon disulfide react to give alkyl mercuric mercaptans.

3. Methylmercuric bicarbonate and *p*-tolylmercuric carbonate have been prepared from the corresponding hydroxides and carbon dioxide. They react with carbon disulfide alone and with alcohol in a manner similar to the corresponding hydroxides.

4. Ethylmercuric-2,4,6-trinitrobenzoate and *p*-tolylmercuric-2,4,6-trinitrobenzoate have been prepared. When heated above the melting point, a molecule of carbon dioxide is lost to form ethylmercuric-2,4,6-trinitrophenyl and *p*-tolylmercuric-2,4,6-trinitrophenyl, respectively.

5. It was found impossible to introduce an alkyl mercury group into organic compounds by means of the alkyl mercuric hydroxides.

URBANA, ILLINOIS

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[10] Rupp, *Chem.-Ztg.*, **32**, 1077 (1908).