[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Mono and Disubstituted Organo-Mercury Derivatives of Acetylene

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We have recently reported[1] the preparation and properties of a series of aryl and normal alkyl mercury acetylides formed by the replacement of both atoms of hydrogen from acetylene by organo-mercury groups. The present paper describes the similar preparation and some variations in the behavior of analogous compounds containing branched alkyl and a few substituted alkyl and aryl groups linked to mercury.

In the preparation of acetylides containing secondary organo-mercury radicals and also of bis-amylmercury acetylide it was noticed after these compounds had been precipitated from alcoholic potassium hydroxide solution, that they could be redissolved by excess acetylene. When the excess acetylene was allowed to escape or was removed by suction, a precipitate separated from solution. In each case comparison of the melting points of purified samples of the two precipitates proved them to be identical, and analysis showed that both hydrogens of acetylene had been replaced by organo-mercury groups.

These acetylides were all very soluble in the common organic solvents, and greater solubility was found to be associated with a more rapid reaction with excess acetylene. It was also found that the more soluble of the normal alkyl mercury acetylides were very slowly redissolved. So it appears that this phenomenon is not due to the presence of any one type of group, but depends solely on the solubility of the bis-organomercury acetylide.

It was found that the presence of alkali in solution catalyzed the formation of the acetylides and their solution in excess acetylene. Thus four minutes elapsed before a precipitate began to appear when acetylene was passed into an alkali-free alcoholic solution of ethylmercury hydroxide prepared by the action of silver hydroxide on ethylmercury chloride in alcohol.[2] An alcoholic potassium hydroxide solution, having the same concentration of ethylmercury chloride, gave the acetylide precipitate immediately. Likewise when the purified acetylides were suspended in alcohol they were slowly attacked by acetylene, while the addition of sodium or potassium hydroxide or even ammonia to these solutions caused the acetylene to dissolve the precipitates much more rapidly.

In order to explain these facts it was assumed that an equilibrium exists between the mono and the bis-organo-mercury acetylides $C_2H_2 + R{-}Hg{-}C{\equiv}C{-}Hg{-}R \rightleftarrows 2\ R{-}Hg{-}C{\equiv}C{-}H$.

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[1] Spahr, Vogt and Nieuwland, THIS JOURNAL, **55**, 2465 (1933).

[2] Dunhaupt, *J. prakt. Chem.*, [1] **61**, 415 (1854).

The catalytic effect of the alkali may possibly be explained as being due to the existence of more acetylide ions in alkaline solution. It has not as yet been found possible to isolate compounds of the type $R—Hg—C\equiv C—H$, but their mode of formation and certain reactions indicate their presence in solution. A reaction of this type is the preparation of isopropylmercury *n*-amyl acetylide formed by the action of *n*-amylacetylene on bis-isopropylmercury acetylide in the presence of excess acetylene.

Marvel and Gould have pointed out[3] that the carbon–mercury linkage $R_2CH—Hg—$ is more easily broken than that in $R—CH_2—Hg—$ by heat and acids. We have found that the same relationship holds with regard to stability toward aqueous alkaline solution. When a secondary organomercury acetylide was prepared in aqueous alkaline solution, it decomposed, splitting out metallic mercury and leaving a black gummy mass from which no crystalline precipitate could be obtained. In an alcoholic alkaline solution prepared from absolute alcohol, the acetylide is stable.

Schoeller and Schrauth[4] have called attention to the fact that α-acetoxymercuri-β-methoxyethane is a powerful vesicant, producing irritating blisters when in contact with the skin. The acetylide of this compound when applied to the skin in undiluted form produced no skin irritation. When heated above its melting point it decomposed, metallic mercury splitting out, leaving behind an oil with a carnation-like odor which solidified on cooling to room temperature. The products of this reaction are at present being investigated.

Experimental Part

Preparation of Organomercury Bromides.—The secondary alkyl mercury, isoamylmercury, and cyclohexylmercury bromides were prepared by converting the organobromide into its Grignard compound, and treating this with an excess of mercuric bromide.[5]

Preparation of *p*-Aminophenylmercury Chloride.—Freshly distilled aniline was treated with mercuric acetate and the *p*-aminophenylmercury acetate which formed was finely powdered and boiled with a large volume of water containing an excess of sodium chloride. Shiny leaflets of *p*-aminophenylmercury chloride separated from solution on cooling.[6]

Preparation of *o*-Nitrophenylmercury Chloride.—Mercuric acetate was heated with five times its weight of nitrobenzene until the solution no longer gave a test with sodium hydroxide. It was allowed to cool and filtered. The filtrate was treated with an excess of sodium chloride solution and steam distilled to remove any unreacted nitrobenzene. The residue was dried and extracted with ligroin, and recrystallized from glacial acetic acid. It was soluble in ether and high boiling ligroin and insoluble in water, m. p. 180–182.°[6]

Preparation of *o*-Hydroxyphenylmercury Chloride.—This was prepared from

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(3) Marvel and Gould, THIS JOURNAL, **45**, 820–823 (1923).

(4) Schoeller and Schrauth, *Ber.*, **46**, 2869 (1913).

(5) Marvel and Calvery, THIS JOURNAL, **45**, 820–823 (1923); Hill, *ibid.*, **50**, 167 (1928); Grüttner, *Ber.*, **47**, 1651–1656 (1914).

(6) Dimroth, *ibid.*, **35**, 2032-2045 (1902).

phenol, mercuric acetate and sodium chloride according to the method of Whitmore and Hanson.[7]

Preparation of Allylmercury Iodide.—This was prepared by the method of Zinin from allyl iodide and metallic mercury.[8]

Preparation of α-Acetoxymercuri-β-methoxyethane.—It was prepared according to the method of Schoeller and Schrauth,[4] as modified by Manchot,[9] and further modified by Ford in this Laboratory.[10]

Ethylene was passed into a solution of one-half mol of mercuric acetate in excess alcohol and one-half mol of mercuric oxide was added at a rate which kept the reaction mixture a faint pink. A Benning gas absorption stirrer[11] was used and the reaction was conducted in a three-necked water-cooled flask, ethylene being supplied by the constant pressure, alarm, gas feeding device described by Vaughn.[12] The reaction was complete in one-quarter hour. After removing the alcohol *in vacuo*, the residue was recrystallized from ether. The melting point was 42°. The yield based on total mercury used was 92.8%.

Preparation of Mercury Acetylides. General Procedure.—They were prepared according to the method outlined in a previous communication,[1] except that a 10% alcoholic solution of potassium hydroxide was used instead of an aqueous solution. The secondary alkyl mercury and the isoamylmercury acetylides were very soluble in the common organic solvents, and were crystallized from ethyl alcohol, giving in each case fine needles. Their melting points are recorded in Table I. The *o*-nitrophenylmercury acetylide is practically insoluble in all organic solvents, and we were unable to purify it by crystallization. Its melting point could not be determined for on heating it above 300°, it decomposed with explosive violence. The *p*-aminophenylmercury acetylide is but slightly soluble in organic solvents. It crystallized in long needles from ethyl alcohol, and turned brown when exposed to the air. Allylmercury iodide, when dissolved in alcoholic ammonia and treated with acetylene, gave a white precipitate which immediately decomposed on exposure to air liberating black metallic mercury.

TABLE I

MERCURIC ACETYLIDES, GENERAL FORMULA $R{-}Hg{-}C{\equiv}C{-}Hg{-}R$

Nature of R	M. p., °C.	Mercury, %	
		Calcd.	Found
Isopropyl	110.5–111.5	78.46	78.18
Sec-butyl	105.5–106	74.38	74.25
Isoamyl	106 –107	70.70	70.72
Cyclohexyl	172 –173	67.84	67.51
β-Methoxyethyl	129.5–130.5 (with dec.)	73.85	73.41
p-Aminophenyl	188 –190 (with dec.)	65.65	66.34
o-Nitrophenyl	Explodes above 300°	59.94	60.99

Method of Analysis.—Mercury was determined according to the method outlined in a previous communication.[1]

Attempted Preparation of *o*-Hydroxyphenylmercury Acetylide.—No acetylide was obtained on passing acetylene into either *o*-hydroxyphenylmercury chloride in alcoholic potash or *o*-hydroxyphenylmercury hydroxide in alcohol. In the latter solution the

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(7) Whitmore and Hanson, "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. IV, 1925, p. 13.

(8) Zinin, *Ann.*, **96**, 353 (1855).

(9) Manchot, *Ber.*, **53**, 986 (1920).

(10) Ford, Thesis, University of Notre Dame, 1933.

(11) Benning, *Proc. Ind. Acad. Sci.*, **37**, 263 (1927).

(12) Vaughn, *J. Chem. Educ.*, **9**, 528 (1932).

final products appeared to be free mercury and phenol which was identified by conversion into picric acid. It is possible that these were formed by the decomposition of an intermediate acetylide.

Preparation of Isopropylmercury Amyl Acetylide.—12.5 g. of isopropylmercury bromide was dissolved in a 10% alcoholic potassium hydroxide solution. Four grams of amylacetylene was added slowly to the isopropylmercury hydroxide which was mechanically stirred. During the addition, the solution assumed a pale yellow color. On the addition of 300 ml. of water to the stirred solution an oil separated and settled to the bottom of the flask. The oil was separated and dried over anhydrous sodium sulfate. It contained a trace of amylacetylene which was removed by distillation under reduced pressure. The crude product weighed 9.2 g. (70% yield). It is an oil with a pale yellow color and of very penetrating odor. It is insoluble in water, but miscible with organic solvents. This material could not be distilled even under 3 cm. pressure on account of decomposition with the formation of free mercury, d_4^{20} 1.628.

Anal. Calcd.: Hg, 59.22. Found: Hg, 58.59.

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Summary

1. The acetylene derivatives of isopropyl, *sec*-butyl, isoamyl, cyclohexyl, *o*-nitrophenyl, *p*-aminophenylmercury halides and α-acetoxymercuri-β-methoxyethane have been prepared and their properties recorded.

2. Isopropylmercury amyl acetylide has been prepared and its properties are recorded.

3. It has been shown that alkalies act as catalyst in the formation of organo-mercury acetylides.

4. Evidence of the existence of mono-mercury acetylides in solution has been given, and it has been shown that the formation of such compounds from the di-mercury acetylides when treated with excess acetylene depends primarily upon the solubility of the di-mercury derivative.

5. Secondary organo-mercury acetylides are unstable in aqueous potassium hydroxide solution, undergoing decomposition with the liberation of mercury.

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