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Summary

The production of azulene and cadalene by dehydrogenation of the sesquiterpene mixture of *Wintera Colorata* has been investigated. Dehydrogenation with sulfur is shown to be selective, all the azulene being formed before any cadalene can be detected.

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Organo-Mercuri Acetylides and their Use in the Identification of Organo-Mercury Halides

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When acetylene is passed into an alkaline solution of mercuric iodide in potassium iodide,¹ a white flocculent precipitate is obtained which has the formula C_2Hg , and which when dry is extremely explosive. Monosubstituted acetylenes react with alkaline solutions of mercuric iodide or cyanide with the formation of salts of the general formula $(R-C\equiv C-)_2Hg$.² Hilpert and Grüttner have reported that pentamethylene-1,5-di-mercurinitrate in alcoholic ammonia solution reacts with acetylene with the formation of pentamethylene-di-mercuri-acetylide.³ While investigating the use of various organic mercury compounds as catalysts in the conversion of acetylene into acetaldehyde, Nieuwland and Toussaint⁴ obtained a white precipitate by the action of acetylene on ethylmercuric chloride in an alcoholic potassium hydroxide solution. The present investigation was undertaken to determine the composition of this and similar compounds and to see whether or not this reaction was general for aliphatic, aromatic and mixed aliphatic-aromatic mercury halides. It was hoped that if the reaction was general, the resulting acetylenic compounds might possess properties which would render them suitable as derivatives for identifying substituted mercury halides.

The action of acetylene on substituted mercury halides in alkaline solution may result in the replacement of one or both of the acetylene hydrogens by organo-mercury groups. Ten different substituted mercury halides were treated with acetylene, and in each case a mercuric acetylide was obtained in good yield. Analysis indicates that in every instance both

(1) Keiser, *Am. Chem. J.*, **15**, 535 (1893).

(2) Johnson and McEwen, *THIS JOURNAL*, **48**, 469 (1926).

(3) Hilpert and Grüttner, *Ber.*, **47**, 184 (1914).

(4) Nieuwland and Toussaint, unpublished work.

acetylenic hydrogens were substituted by mercury. These compounds were white crystalline solids and possessed sharp melting points. The melting points of the new mercuric acetylides and their formulas are listed in Table I. In structure these compounds resemble cuprous and silver acetylide, but differ in that they are soluble in organic solvents and are volatile. They possess an odor resembling that of garlic. They are unstable and decompose on exposure to air. The rate of decomposition varies widely, depending on the group attached to mercury. The phenylethyl derivative decomposes immediately on forming and a layer of phenylacetaldehyde collects on the surface of the reaction mixture. On standing in the presence of a trace of moisture, the benzyl derivative decomposes with the formation of benzaldehyde. The *o*- and *p*-tolyl and phenyl derivatives are very stable and can be kept for months without noticeable decomposition. The stability of the alkyl derivatives decreases as the molecular weight of the alkyl group increases.

The procedure used in the preparation of these derivatives consisted in passing acetylene into an alkaline solution of substituted mercury halides. A white precipitate immediately forms which is filtered, washed with water and 70% alcohol, and purified by crystallization. The yields of the crude products were usually between 80–90%. The formation of a white precipitate by the action of acetylene is a delicate test for alkyl and aryl mercury halides when dissolved in dilute aqueous potassium hydroxide solution. One cg. of a substituted mercury halide dissolved in 10 ml. of potassium hydroxide solution and treated with acetylene gave a precipitate sufficient for purification and melting point determination.

Experimental Part

Preparation of Alkyl and Aryl Mercury Halides.—These were prepared, with the exception of ethylmercury chloride, by the action of alkyl and aryl Grignard reagents with an excess of the corresponding mercuric halide.⁵ The ethylmercury chloride was of commercial grade and was purified by two crystallizations from ethyl alcohol.

Preparation of Acetylenic Mercury Derivatives. General Procedure.—These compounds were prepared from the bromide except in the case of the methyl derivative, which was prepared from the iodide, and the ethyl and benzyl derivatives, which were prepared from the chloride. Eight grams of pure substituted mercury halide was dissolved in 800 ml. of a 10% aqueous solution of potassium hydroxide contained in a liter Florence flask. The clear solution was treated with acetylene in a closed system. The solution immediately became turbid and a white precipitate separated which settled to the bottom of the reaction flask. Gas was passed in, with occasional shaking of the flask, until the solution no longer absorbed acetylene. The precipitate was filtered with suction, washed well with water to remove any potassium halide, and then with a little 70% alcohol. The crude products were crystallized from the solvents specified in Table I. With the exception of the ethyl and benzyl derivatives which formed platelets, all the other derivatives crystallized as shiny needles. They are easily soluble in pyridine and soluble in hot benzene and carbon tetrachloride.

(5) Marvel, Gauerke and Hill, *THIS JOURNAL*, **47**, 3009–11 (1925).

TABLE I
MERCURY ACETYLIDES, GENERAL FORMULA R—Hg—C≡C—Hg—R

Substance	Recrystallized from	M. p. of compound (uncorr.), °C.	Mercury, % Calcd.	Found
CH ₃ HgC≡CHgCH ₃	Acetone	232–233 ^c	88.12	88.21
C ₂ H ₅ HgC≡CHgC ₂ H ₅	Pyridine	195–196	82.58	82.61
C ₃ H ₇ HgC≡CHgC ₃ H ₇	MeOH	150–151	78.46	78.59
C ₄ H ₉ HgC≡CHgC ₄ H ₉	Acetone ^a	125.5–126.5	74.38	74.51
C ₆ H ₁₁ HgC≡CHgC ₆ H ₁₁	MeOH	91–92	70.70	70.59
C ₆ H ₁₃ HgC≡CHgC ₆ H ₁₃	EtOH	104–105	67.38	67.40
C ₆ H ₅ HgC≡CHgC ₆ H ₅	Carbon tet. ^b	179–180 ^e	69.25	69.09
C ₆ H ₄ CH ₃ HgC≡CHgCH ₃ C ₆ H ₄ ^c	Benzene	205–206	66.06	65.92
C ₆ H ₄ CH ₃ HgC≡CHgCH ₃ C ₆ H ₄ ^d	Benzene	190–191	66.06	66.00
C ₆ H ₅ CH ₂ HgC≡CHgCH ₂ C ₆ H ₅	Carbon tet.	110–111	66.06	65.87

^a To obtain crystals the solution must be allowed to cool slowly. ^b The solution has a tendency to remain supersaturated, but crystallization takes place if the solution is allowed to stand for several hours. ^c *o*-Tolylmercury acetylide. ^d *p*-Tolylmercury acetylide. ^e With previous darkening.

Attempted Preparation of Phenylethylmercury Acetylide.—Attempts were made to prepare this compound from phenylethylmercury bromide by the same procedure as used above. When acetylene was passed into the solution of phenylethylmercury hydroxide a turbidity was produced and after a few minutes a layer of oil collected on the surface, a black gummy mass settling to the bottom of the flask. The oil was separated by extraction with two portions of ether. The ether was removed by distillation and the oil which remained converted into its hydrazone by treatment with phenylhydrazine. The m. p. was 55.5°. The m. p. of the hydrazone of phenylacetaldehyde has been reported as 58°. No crystalline product was obtained from the gummy solid.

Proof of Acetylenic Structure.—That these compounds contain a triple bond is shown by the following reactions. (1) When 3 ml. of concd. hydrochloric acid is added to 0.1 g. of any alkyl or aryl mercury acetylide and heated and the gas which is formed passed into an ammoniacal solution of cuprous chloride, cuprous acetylide is precipitated.⁷ (2) The addition of a few crystals of iodine to 0.1 g. of any alkyl or aryl mercury acetylide dissolved in benzene yields diiodoacetylene, the mercury splitting out as mercuric iodide.

Method of Analysis.—The mercuric acetylenic compounds were decomposed according to the method of White,⁸ and titrated according to the method of Rupp.⁹

A 0.2-g. sample of the mercury compound was decomposed with 10 ml. of concd. sulfuric acid. Potassium permanganate was added in small amounts until the color of the mixture was finally dark brown. The excess permanganate was removed by oxalic acid and hydrogen peroxide. Ferric alum indicator was added to the clear solution, the volume made up to 100 ml., and the mercury titrated with 0.1 *N* potassium thiocyanate.

Work is at present being carried out in this Laboratory on the action of acetylene on alkaline solutions of substituted phenylmercury halides, and secondary alkyl mercury halides.

(6) Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 20.

(7) Mulliken, Ref. 6, p. 199.

(8) White, THIS JOURNAL, **42**, 2355–2366 (1920).

(9) Rupp, Chem.-Ztg., **32**, 1077 (1908).

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Summary

1. It has been found that alkyl and aryl mercury halides in alkaline solution react with acetylene with the formation of soluble mercury acetylides of the general formula $R-Hg-C\equiv C-Hg-R$.

2. The acetylene derivatives of methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, phenyl, *o*-tolyl, *p*-tolyl and benzylmercury halides have been prepared and their properties recorded.

3. Since these acetylenic derivatives are easily prepared and purified and possess sharp melting points, they are suitable derivatives for the identification of organo-mercury halides.

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The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. I. The Addition of Hydrogen Bromide to Allyl Bromide

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Introduction

The theory of partial polarity of the ethylene bond proposed by one of us³ postulates that in unsymmetrical ethylene compounds, one of the two electron pairs constituting the double bond is held in common by the two carbon atoms concerned and the other behaves as if it were decidedly closer to one of the carbon atoms than to the other. It is an essential part of the theory also that this second electron pair lies closer in general to that carbon atom which carries the least electronegative radicals. In view of some discrepancies between the predicted and the experimentally recorded results, it became necessary to repeat the work on the addition of hydrogen bromide to allyl bromide and many other unsaturated compounds. In the course of this work, the effect of peroxides on the direction of addition was discovered. This paper deals with the magnitude of that effect on the addition of hydrogen bromide to allyl bromide, but

(1) This communication is an abstract of a dissertation submitted by Frank R. Mayo in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Chicago, 1931. A part of this work was presented at the Cincinnati meeting of the American Chemical Society, September, 1930.

(2) The authors wish to take this opportunity to express their appreciation to the Eli Lilly Company of Indianapolis for support which made this work possible.

(3) Kharasch and Darkis, *Chem. Rev.*, **5**, 571 (1928); Kharasch and Reinmuth, *J. Chem. Education*, **8**, 1703 (1931).