[CONTRIBUTION NO. 125 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XVII. Mercury Derivatives of Vinylacetylene

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As a means of identifying true acetylenic compounds the derivatives formed by the action of K_2HgI_4 are useful since they are generally crystalline and have definite melting points.[1] When this reagent is applied to vinylacetylene (I) it furnishes di-vinylethynyl-mercury (II), which separates from alcohol in the form of white leaflets melting at 144 to 145°. The compound is readily soluble in chloroform, but on standing in the air for twenty-four to forty-eight hours it becomes yellow in color and insoluble in chloroform. Analysis indicates that considerable amounts of oxygen are absorbed during this transformation. The oxidized product does not melt, but sometimes explodes on being heated or subjected to mechanical shock.

Di-vinylethynyl-mercury undergoes the following transformations. Cold dilute hydrochloric acid regenerates the vinylacetylene; chlorine and bromine yield the α-chloro- and bromo-vinylacetylenes (III); and metallic sodium in dry benzene produces sodium vinylacetylide.

Di-vinylethynyl-mercury is also produced by the action of mercuric acetate in acetic acid on vinylacetylene at ordinary temperatures, but if the temperature is raised to 60 or 70° reaction proceeds further with the formation of a compound whose composition and chemical behavior agree with that required for 1,1-di-acetoxymercuri-2-acetoxymercurioxy-1,3-butadiene (IV). The same product is obtained by treating di-vinylethynyl-mercury with mercuric acetate in acetic acid at 60 to 70°.[2]

$CH_2{=}CH{-}C{\equiv}CH$ (I)

$(CH_2{=}CH{-}C{\equiv}C)_2Hg$ (II)

$CH_2{=}CH{-}C{\equiv}CX$ (III)

$CH_2{=}CH{-}(CH_3COOHgO)C{=}C(HgOOCCH_3)_2$ (IV)

$CH_2{=}CH{-}CO{-}CH_3$ (V)

$CH_2{=}CH{-}CO{-}CBr_3$ (VI)

$CH_2{=}CH{-}(OHgX)C{=}C(HgX)_2$ (VII)

This compound is a white crystalline solid somewhat soluble in water and more soluble in dilute acetic acid. It is infusible. By the action of hydrochloric acid it is decomposed with the formation of methyl vinyl ketone (V). Similarly by the action of bromine it is converted into tribromomethyl vinyl ketone (VI). The action of potassium iodide, bromide or chloride on IV causes replacement of the acetyl groups by halogen

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[1] Johnson and McEwen, THIS JOURNAL, **48**, 469 (1926).

[2] Myddleton, Barrett and Seager, *ibid.*, **52**, 4405 (1930), have presented evidence favoring the general structure $-C(OHgOAc){=}C(HgOAc)_2$ for the products obtained by the action of mercuric acetate on monosubstituted acetylenes.

and gives insoluble products corresponding in composition with the general formula VII.

Di-vinylethynyl-mercury.—The addition of an alcoholic solution of vinylacetylene to an excess of the alkaline mercuric iodide reagent[1] yielded a copious precipitate. This was filtered off and crystallized from boiling absolute alcohol. It separated in the form of white leaflets melting at 144 to 145°.

Anal. Calcd. for C_8H_6Hg: Hg, 66.25. Found: Hg, 66.46, 66.35.

The same compound was obtained by adding vinylacetylene (30 g.) to a cold solution of 5 g. of mercuric oxide in 250 cc. of acetic acid.

Anal. Calcd. for C_8H_6Hg: C, 31.72; H, 1.99. Found: C, 32.00; H, 2.46.

Upon standing for forty-eight hours the di-vinylethynyl-mercury became yellow in color and insoluble in chloroform. It had also acquired the ability to explode under the action of heat or mechanical shock. Analysis of this explosive product showed the presence of only 27.70% carbon and 2.23% hydrogen.

Freshly prepared di-vinylethynyl-mercury reacted with bromine or iodine to give the corresponding bromo- and iodo-vinylacetylenes. In one experiment 23.5 g. of the mercury compound in 177 cc. of chloroform was treated slowly with a 10% solution of bromine in chloroform; 22.64 g. of bromine was absorbed before decolorization ceased. The chloroform was removed, and distillation of the residue (11 g.) then gave 3 g. of 1-bromo-2-vinylacetylene, b. p. 50 to 52° at 210 mm. (see p. 4667).

1,1-Di-acetoxymercuri-2-acetoxymercurioxy-1,3-butadiene (IV).—A solution of 5.2 g. of vinylacetylene in 100 cc. of acetic acid was added to a solution of 86.6 g. of mercuric oxide in 700 cc. of acetic acid surrounded by a water-bath at 45°. After one-half hour the temperature of the bath was increased to 60° and maintained between 60–70° for four hours. During this period a white crystalline solid separated. The mixture was filtered and the solid (79 g.) crystallized from dilute acetic acid; yield 93.4%. The product was somewhat soluble in water, more so in dilute acetic acid, but insoluble in the common organic solvents.

Anal. Calcd. for $C_{10}H_{12}O_7Hg_3$: C, 14.18; H, 1.43; Hg, 71.15. Found: C, 14.14; H, 1.95; Hg, 70.72.

1,1-Di-iodomercuri-2-iodomercurioxy-1,3-butadiene.—To a hot solution of 4 g. of 1,1-diacetoxymercuri-2-acetoxymercurioxy-1,3-butadiene in 100 cc. of 50% acetic acid was added slowly with stirring 2.8 g. of potassium iodide in 20 cc. of water. The yellow precipitate was filtered, washed several times with hot 50% acetic acid, then with water, and finally with acetone. The pale yellow solid was insoluble in water and in the common organic solvents.

Anal. Calcd. for $C_4H_3OHg_3I_3$: Hg, 57.34; I, 36.28. Found: Hg, 55.22, 55.47; I, 36.27, 36.45.

1,1-Di-bromomercuri-2-bromomercurioxy-1,3-butadiene was obtained in a similar manner from potassium bromide as a white solid insoluble in water and in the common organic solvents.

Anal. Calcd. for $C_4H_3OHg_3Br_3$: Hg, 66.23; Br, 26.37. Found: Hg, 67.82, 68.14; Br, 25.18, 25.29.

1,1-Di-chloromercuri-2-chloromercurioxy-1,3-butadiene was obtained in a similar manner from potassium chloride as a white solid insoluble in water and in the common organic solvents.

Anal. Calcd. for $C_4H_3OHg_3Cl_3$: Cl, 13.72. Found: Cl, 14.38.

Hydrolysis of 1,1-Di-acetoxymercuri-2-acetoxymercurioxy-1,3-butadiene.—To 423 g. of the mercury compound (0.5 mole) in 200 cc. of water was added 300 cc. of hydrochloric acid (37%). After three hours, a small amount of hydroquinone was added, and the solution distilled until the distillate amounted to 300 cc. From the latter, pure methyl vinyl ketone was isolated by ether extraction and distillation. With phenylhydrazine it gave the known derivative phenyl-1-methyl-3-pyrazoline melting at 76°.[3]

Action of Bromine on 1,1-Di-acetoxymercuri-2-acetoxymercurioxy-1,3-butadiene.—Bromine (239 g.) was slowly added to a suspension of 285 g. (0.337 mole) of the mercury compound in 700 cc. chloroform until decolorization was complete. Cooling was required to maintain the temperature below 60°. After standing, the mixture was filtered, washed with 10% hydrochloric acid and with water and distilled. At 0.5 mm. 44 g. of a yellow viscous liquid boiling at 128–130° was obtained. On standing for forty-eight hours it solidified. Three crystallizations from petroleum ether gave white rectangular plates melting at 73–75°. Although additional crystallizations did not alter the melting point, the product was not analytically pure. However, the ease with which bromoform was liberated when the crystals were warmed with dilute alkali indicates that the product was mainly tribromomethyl vinyl ketone contaminated perhaps with dibromomethyl vinyl ketone.

Anal. Calcd. for $C_4H_3OBr_3$: C, 15.64; H, 0.98; Br, 78.15. Found: C, 16.42, 16.85; H, 1.89, 1.75; Br, 72.18, 71.89.

Summary

Vinylacetylene when treated with potassium mercuri-iodide or with mercuric acetate at the ordinary temperature yields di-vinylethynyl-mercury, a crystalline solid melting at 144 to 145°. The action of mercuric acetate on vinylacetylene at 60 to 70° yields 1,1-di-acetoxymercuri-2-acetoxymercurioxy-1,3-butadiene. Some reactions of these compounds are described.

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[3] Maire, *Bull. soc. chim.*, (4) **3**, 272 (1908).

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RECEIVED JULY 21, 1933
PUBLISHED NOVEMBER 7, 1933

[CONTRIBUTION NO. 126 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & CO.]

Acetylene Polymers and their Derivatives. XVIII. 1-Halogen-2-vinylacetylenes

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By the action of alkaline hypohalites, true acetylenic hydrogens are generally replaced by halogen.[1] This reaction has now been applied to vinylacetylene, and the 1-halogen-2-vinylacetylenes whose properties are listed in Table I have been prepared. In a general way they resemble other halogen acetylenes. They are liquids with highly characteristic repulsive sickening odors. Under diminished pressure in an atmosphere of nitrogen they can be distilled, but dangerous explosions occur if air is present, or if heating of the residue is carried too far. A sample of the chloro compound in one instance inflamed spontaneously when a specimen was being removed for analysis.

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[1] Straus, Kollek and Heyn, *Ber.*, **63**, 1868 (1930).