chloric 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.

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

WILMINGTON, DELAWARE

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

BY RALPH A. JACOBSON AND WALLACE H. CAROTHERS

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.

---

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

The compounds when freshly distilled are colorless but they darken on standing and are finally transformed into black, brittle solids. These solids are sensitive to heat and percussion and they explode with considerable violence. The product from the iodo compound is the most sensitive and violent; that from the chloro compound the least.

PHYSICAL PROPERTIES OF $CH_2{=}CH{-}C{\equiv}C{-}X$

Nature of X	B. p., °C.	n_D^{20}	d_4^{20}	MR_D calcd.	MR_D found	Exaltation
Cl	55 to 57 at 760 mm.	1.4663	1.0032	22.94	23.89	0.95
Br	52 to 53 at 217 mm.	1.5182	1.4804	25.81	26.80	.99
I	78 at 125 mm.	1.5948	1.8968	31.07	31.88	.81

The bromo compound was formed rather rapidly when vinylacetylene was treated with potassium hypobromite; hypochlorite acted very much more slowly and the yields of the chloro compound were rather low. In preparing the iodo compound a solution of iodine in potassium iodide was used. The iodo and bromo compounds have also been obtained[2] by the action of iodine and bromine on di-vinylethynyl-mercury. The iodo compound was also formed when vinylethynylmagnesium bromide was treated with iodine. Since a deficiency of iodine was used, it appears that the tendency of the iodo compound to react with the Grignard reagent is very slight.

In alcoholic solution the iodo compound adds one molecule of hydrogen chloride. This reaction was carried out in the expectation that the product would be the substituted chloroprene, $CH_2{=}CH{-}CCl{=}CHI$. The product did indeed polymerize spontaneously, but it yielded only a sticky black tar and no attempt was made to confirm its structure.

Experimental Part

Preparation of 1-Bromo-2-vinylacetylene.—Bromine (80 g.) was added at 0° to 180 g. of potassium hydroxide in 800 g. of water. Then 30 g. of vinylacetylene was added during one-half hour with stirring under nitrogen. After two hours a heavy oily layer separated. This was dried with calcium chloride and distilled under reduced pressure of nitrogen. Some vinylacetylene was recovered, and then 36.4 g. (55%) of 1-bromo-2-vinylacetylene was collected between 52 and 53° at 217 mm. A small amount of liquid remaining in the distilling flask exploded when further distillation was attempted. The bromovinylacetylene though colorless at first, quickly became yellow and then progressively darker upon standing. Its odor was nauseating and exposure to its vapors caused headaches. A specimen stabilized with hydroquinone did not polymerize within a month. When examined several months later it was a highly explosive black solid.

Anal. Calcd. for C_4H_3Br: C, 36.66; H, 2.27, mol. wt., 130.9. Found: C, 36.72, H, 2.46; mol. wt., 131, 136 (cryoscopic, benzene).

Preparation of 1-Iodo-2-vinylacetylene.—To a solution of 84 g. (1.5 mole) of potassium hydroxide in 1000 g. water at 0°, 65 g. of vinylacetylene was added and then, with

---

[2] Carothers, Jacobson and Berchet, THIS JOURNAL, **55**, 4665 (1933); Vaughn and Nieuwland, *ibid.*, **55**, 2150 (1933), report that iodovinylacetylene is obtained from iodine and vinylacetylene in liquid ammonia.

vigorous stirring during two hours, a solution of 140 g. of potassium iodide and 127 g. of iodine in 110 cc. of water. After standing overnight, the 1-iodo-2-vinylacetylene (95 g.) which had separated to the bottom was removed, dried with calcium chloride, and distilled under reduced pressure of nitrogen; yield, 49 g. or 27.5%. The compound was at first colorless, but on standing it became reddish-brown. After a month at 10° it had polymerized to a jelly, and after several months to a black solid similar in appearance to charcoal. This polymer was extremely explosive.

Anal. Calcd. for C_4H_3I: C, 26.97; H, 1.69; mol. wt., 177.95. Found: C, 27.30; H, 1.75; mol. wt., 181 (cryoscopic, benzene).

The iodo compound was also obtained by the action of iodine on vinylethynylmagnesium bromide. To an ethereal solution containing one mole of the reagent, 127 g. (one gram atom) of iodine was slowly added. A smooth reaction occurred and the iodine instantly dissolved with decolorization. A small test sample was removed and found to take up considerably more iodine. However, the main portion was distilled in vacuum and a liquid boiling at 82 to 83° at 150 mm. was collected. This agreed in odor and physical constants with the 1-iodo-2-vinylacetylene described above.

Preparation of 1-Chloro-2-vinylacetylene.—Some difficulty was at first experienced in obtaining this compound, but with the following procedure it was isolated in yields of about 10%. To a solution of 500 g. of potassium hydroxide in 1800 cc. of water at 0° were added 225 g. of chlorine and then 300 g. of vinylacetylene. The mixture was stirred for eight hours. After standing overnight the upper layer (47 g.) was separated, dried with calcium chloride, and distilled under nitrogen. Two distillations gave 23 g. of 1-chloro-2-vinylacetylene boiling at 55 to 57°. It had a nauseating odor and, while colorless at first, it darkened on standing and ultimately polymerized to a black, brittle resinous solid.

Anal. Calcd. for C_4H_3Cl: C, 55.49; H, 3.49; mol. wt., 86.5. Found: C, 55.28; H, 4.06; mol. wt., 87, 89 (cryoscopic, benzene).

Addition of Hydrogen Chloride to 1-Iodo-2-vinylacetylene.—A solution of hydrogen chloride (38 g.) in 95% alcohol was mixed in a pressure bottle with 49 g. of 1-iodo-2-vinylacetylene, 10 g. of ammonium chloride, and 15 g. of cuprous chloride. The bottle was shaken for twenty-four hours at 25° and the oily layer was distilled first with steam and then under nitrogen. The distillate was red in color and boiled at 73.5–74.5° at 35 mm.; yield, 26 g. (44%); d^{20}_{4}, 1.9161; n^{20}_{D} 1.6073.

Anal. Calcd. for C_4H_4ICl: C, 22.38; H, 1.88; total silver halide, 0.1704 g., mol. wt., 214.4. Found: C, 22.34; H, 2.07; total silver halide, 0.1699 g.; mol. wt., 225, 228 (cryoscopic, benzene).

Upon standing for several months the compound polymerized to a soft black tar.

The addition of hydrogen chloride to 1-bromo-2-vinylacetylene under similar conditions also gave a volatile product which polymerized on standing.

Summary

The acetylenic hydrogen of vinylacetylene has been replaced by bromine, iodine and chlorine and the corresponding 1-halogen-2-vinylacetylenes obtained. These compounds are unstable liquids which polymerize upon standing to black solid polymers. The latter are explosive when heated or submitted to mechanical shock. Addition of hydrogen chloride to the iodo compound yielded an addition product which also polymerized spontaneously.

WILMINGTON, DELAWARE

RECEIVED JULY 21, 1933
PUBLISHED NOVEMBER 7, 1933