Summary

1. The action of iodine monochloride with several organic mercury compounds has been studied.
2. The products obtained are organic iodides except when a secondary reaction with the iodine chloride converts the organic iodide to a chloride.
3. The yields of organic iodides obtained are sufficiently high to justify the use of iodine monochloride in place of iodine in converting organic mercury compounds to organic iodides.

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RECEIVED AUGUST 11, 1932
PUBLISHED FEBRUARY 9, 1933

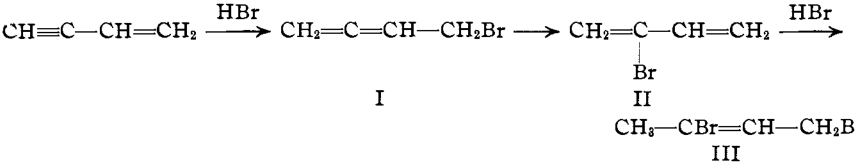
[CONTRIBUTION NO. 106 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. IV. The Addition of Hydrogen Bromide to Vinylacetylene, Bromoprene and Dibromobutene

BY WALLACE H. CAROTHERS, ARNOLD M. COLLINS AND JAMES E. KIRBY

Observations on the combination of vinylacetylene with hydrogen chloride[1] have been extended to the analogous case of hydrogen bromide.

The two reactants are closely similar in their behavior, but hydrogen bromide appears to act somewhat more slowly than hydrogen chloride. Concentrated aqueous hydrobromic acid containing cuprous bromide, when shaken with vinylacetylene at the ordinary temperature, yields the two products, bromo-2-butadiene-1,3 (bromoprene, II) and dibromo-2,4-butene-2 (III). It seems likely, in view of the results already described for the hydrogen chloride reaction[1b] that the primary product of reaction between hydrogen bromide and vinylacetylene is bromo-4-butadiene-1,2 (I), which then rearranges to yield bromoprene, but no decisive direct evidence for the formation of this primary product is yet available. Its presence among the reaction products has not been established—even when no cuprous bromide (catalyst) was used. The structure of the dihydrobromide has not yet been directly established either, but formula III, in view of the results with hydrogen chloride, is not open to serious doubt.



$$CH\equiv C—CH=CH_2 \xrightarrow{HBr} \underset{I}{CH_2=C=CH—CH_2Br} \longrightarrow \underset{II}{CH_2=\underset{Br}{C}—CH=CH_2} \xrightarrow{HBr} \underset{III}{CH_3—CBr=CH—CH_2Br}$$

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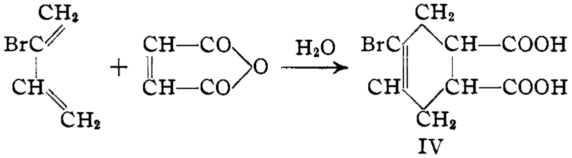
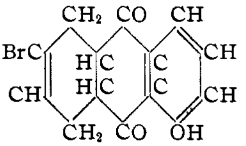
[1] (a) Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4203 (1931); (b) Carothers, Berchet and Collins, *ibid.*, **54**, 4066 (1932).

The third step in this series of reactions has a relatively high velocity, and appreciable amounts of the dihydrobromide (III) are present in the reaction mixture even at an early stage when the major part of the vinylacetylene applied remains unchanged. In this respect also the behavior of hydrogen bromide appreciably differs from that of hydrogen chloride.

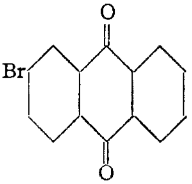
Bromoprene is an oil having a faint greenish-yellow color and an odor rather closely resembling that of butyl bromide. It boils at 42 to 43° at 165 mm. The proof of its structure follows the course already indicated for chloroprene. It reacts with maleic anhydride to yield, after hydrolysis, a product whose composition agrees with that required for bromo-6-cyclohexene-5-dicarboxylic-2,3 acid (IV). Bromoprene furthermore reacts readily with naphthoquinone. The primary product is a crystalline solid, which probably has the formula bromo-2-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (V). It is rapidly oxidized by air in alkaline solution to β-bromoanthraquinone (VI).



IV



V



VI

Experimental Part

Preparation of Bromoprene.—Fifty grams of cold vinylacetylene was placed in a pressure bottle containing 225 cc. of a thoroughly chilled solution prepared by dissolving 75 g. of moist, freshly prepared cuprous bromide in 200 g. of concentrated hydrobromic acid (sp. gr. 1.55). The bottle was allowed to warm up to room temperature and was then mechanically shaken for seven hours. After standing overnight and shaking for another two hours the unused vinylacetylene was allowed to evaporate. The residual oil was separated, washed with water, dried over calcium chloride and distilled from hydroquinone under reduced pressure. Dry, oxygen-free nitrogen was led through the capillary tube during the distillation. The yield of bromoprene boiling at 42–43° at 165 mm. was 30 g. (24%); d_4^{20}, 1.397; n_D^{20} 1.4988; M_R calcd., 27.50; M_R found, 27.94.

Anal. Calcd. for C_4H_5Br: C, 36.11; H, 3.78; Br, 60.15. Found: C, 36.32, 36.47; H, 4.13, 4.21; Br, 60.91, 61.43.

Higher yields were obtained by the use of more concentrated hydrobromic acid. For example, by using 2 moles of hydrobromic acid (sp. gr. 1.66) for each mole of vinylacetylene a yield of 44.8% of bromoprene was obtained.

Dibromo-2,4-butene-2.—After the distillation of the bromoprene a considerable amount of higher-boiling residue remained. From this residue there was obtained 12 g.

(6%) of a strongly lachrymatory, light yellow oil corresponding in analysis to a dibromobutene. It had the following physical constants: b. p. (760 mm.) 168 to 169° with loss of HBr; b. p. (23 mm.) 73°; d_4^{20} 1.8768; n_D^{20} 1.5485; M_R calcd., 35.74; M_R found, 36.25.

Anal. Calcd. for $C_4H_6Br_2$: C, 22.43; H, 2.80; Br, 74.77. Found: C, 22.98, 23.06; H, 3.05, 2.95; Br, 74.94, 75.34.

Reaction of Bromoprene with Maleic Anhydride. Preparation of Bromo-6-cyclohexene-5-dicarboxylic-2,3 Acid.—To 5 g. (0.037 mole) of bromoprene was added 3 g. (0.030 mole) of maleic anhydride. After the mixture had stood at room temperature for about one hour a spontaneous reaction set in and after three or four hours the mass solidified. The reaction product was then dissolved in benzene and shaken for twenty minutes with an excess of 10% sodium hydroxide. The aqueous layer was separated and acidified. The crude acid which separated was purified by recrystallization from water. It separated from water in the form of a mixture of thick plates and blunt needles melting sharply at 186.5 to 187°.

Anal. Calcd. for $C_8H_9O_4Br$: C, 38.57; H, 3.64; neutral equivalent, 124.5. Found: C, 38.37, 38.65; H, 3.75, 3.65; neutral equivalent, 125.4.

Action of α-Naphthoquinone on Bromoprene. Conversion to β-Bromoanthraquinone.—To a benzene solution of 15.4 g. (0.12 mole) of bromoprene was added 10 g. (0.06 mole) of α-naphthoquinone. After standing at room temperature for two days the solution was gently refluxed for one hour. The benzene was then distilled off under reduced pressure. The residual sticky, dark red solid was pressed on a porous tile and then extracted with warm alcohol. The alcohol was decanted from an insoluble tar and, on cooling, 4.9 g. (49%) of unchanged naphthoquinone crystallized out. When the alcohol mother liquor was diluted with water, 2.6 g. of a nearly black solid separated. After recrystallization from alcohol it was obtained in the form of small, soft, nearly white crystals. When slowly heated on a copper block it began to turn blue at about 115° and slowly deepened in color as the temperature was raised. At 138° it melted sharply; as the temperature was raised further it volatilized completely.

The analyses corresponded with the values calculated for bromo-2-tetrahydro-1,4,4a,8a-anthraquinone-9,10.

Anal. Calcd. for $C_{14}H_{11}O_2Br$: C, 57.74; H, 3.99. Found: C, 57.66, 57.65; H, 3.89, 4.04.

About 0.1 g. of the substance was dissolved in alcohol and a few drops of 10% sodium hydroxide solution added. The solution was dark red in color. As air was bubbled through the solution, the red color gave way to green, which in turn disappeared leaving a yellow solid. After recrystallization from amyl alcohol the oxidation product melted at 205–207°. β-Bromoanthraquinone melts at 207°.[2]

Summary

Vinylacetylene reacts with aqueous hydrobromic acid to form bromo-2-butadiene-1,3 (bromoprene) and dibromo-2,4-butene-2. Bromoprene reacts with maleic anhydride yielding bromo-6-cyclohexene-5-dicarboxylic-2,3 acid, and with naphthoquinone yielding a bromotetrahydroanthraquinone which is readily oxidized to β-bromoanthraquinone.

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RECEIVED AUGUST 11, 1932
PUBLISHED FEBRUARY 9, 1933

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(2) Heller, *Ber.*, **45**, 672 (1912).