apparent pH values, in a flavonoid: copper ratio of 1:1.

The results show a glucoluteolin: copper ratio of 2:1 at pH 6.5, but 1:1 at pH 10. The same was found for dihydroquercetin. These indicate the importance of the pH factor in the resulting ratio of flavonoid to copper and possibly may indicate the participation of one potential chelating site at the more acid pH and two sites at the higher pH. Grimaldi and White,[5] in a recent study on the use of quercetin as a colorimetric reagent for determination of zirconium, likewise reported that the mole ratio of quercetin to zirconium in the complex could be either 2:1 or 1:1, depending on experimental conditions.

As shown in Tables II and IV, both butin and 1-epicatechin apparently fail to complex copper at a pH near neutrality, but do so at higher pH values.

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NORMAN, OKLAHOMA

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[5] F. S. Grimaldi and C. E. White, Abstracts, 124th A.C.S. Meeting, 3B (Sept., 1953).

NOTES

Acetylenes. I. Mixed Dihalides and Halohydrins from Butynediol[1]

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In a research program designed to study the effect of structure on the properties of hydrocarbon polymers,[4] polydimethyleneacetylene was desired not only to determine the effect of triple bonds on the properties of a polymer but also to serve as a source for the synthesis of all-*cis*- and all-*trans*-polybutadiene. The most logical starting material for the synthesis of this acetylene polymer appeared to be some derivative of the readily available 2-butyne-1,4-diol (I).

Johnson[5] found that 1,4-dichloro-2-butyne (II) would not react with magnesium to form a Grignard reagent or a polymer. Apparently the chlorine atoms, although reactive to nucleophilic displacements, are not reactive enough to free radical attack by magnesium to form a Grignard reagent under ordinary conditions. Johnson[5] also found that 1,4-dibromo-2-butyne (III) would not form a Grignard reagent. Apparently the first trace of Grignard reagent was extremely reactive and coupled with itself to coat the magnesium with a thin coating of a polymer, preventing any further reaction. It appeared, then, that if the dichloro compound II was not reactive enough to form a Grignard and the dibromo derivative III was too reactive, some mixed dihalide should have an intermediate reactivity so that one halo group would form a Grignard but the other halo group would not immediately couple with it. Three mixed dihalides were synthesized and their reactivities were studied.

Treatment of 2-butyne-1,4-diol (I) with a slight excess of thionyl chloride in pyridine produced a 61% yield of 4-chloro-2-butyne-1-ol (IV) plus a 15% yield of the 1,4-dichloro-2-butyne (II). Since the chlorohydrin IV was comparatively easy to prepare, it was used as the starting material for the other halohydrins. Thus, IV plus sodium bromide in methanol gave a 62% yield of 4-bromo-2-butyne-1-ol (V), while IV plus sodium iodide in acetone gave a 95% yield of the solid 4-iodo-2-butyne-1-ol (VI). IV reacted only slowly with alcoholic silver nitrate, while both V and VI gave an immediate precipitate with the same reagent.

Reaction of the chlorohydrin IV with phosphorus tribromide in chloroform produced a 70% yield of 1-chloro-4-bromo-2-butyne (VII). Similarly, the iodohydrin VI plus phosphorus trichloride produced a 37% yield of the highly reactive 1-chloro-4-iodo-2-butyne (VIII), while VI plus phosphorus tribromide gave a 90% yield of the solid 1-bromo-4-iodo-2-butyne (IX).

When the chlorobromo derivative VII was treated with magnesium in ether, a Grignard reagent resulted. The presence of the Grignard reagent was indicated by the violent reaction upon the addition of water and the formation of color with Michler ketone.[6] Apparently, it is the bromo group of VII that is reactive enough to form the Grignard, confirming Johnson's explanation of the lack of formation of a Grignard reagent with dibromobutyne III. In a similar manner, the chloroiodo compound VIII would form a Grignard, but the 1-bromo-4-iodo-2-butyne (IX) would not. Apparently, IX behaved very much like III in this reaction.

In view of the recent[7] synthesis of butatriene by treatment of III with zinc in diethylene glycol diethyl ether at 80°, the formation of the Grignard reagent from VII is extremely interesting. Ap-

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[1] Presented in part at the 118th Meeting of the American Chemical Society, Chicago, Ill., September, 1950.

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[3] Office of Naval Research Fellow, 1949–1951.

[4] W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 5418 (1954).

[5] A. W. Johnson, *J. Chem. Soc.*, 1009 (1946).

[6] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1952).

[7] W. M. Schubert, T. H. Liddicoet and W. A. Lanks, *ibid.*, **75**, 1929 (1954).

parently there is no strong driving force for this Grignard to lose the elements of magnesium chloride bromide to form butatriene. The Grignard solution derived from VII or VIII produced a polymeric precipitate on standing. The structure of this polymer will be the subject of a subsequent paper.

Experimental[8]

4-Chloro-2-butyne-1-ol (IV).—To a solution of 860 g. (10 moles) of 2-butyne-1,4-diol (I) in 1 liter of dry benzene and 869 g. (11 moles) of dry pyridine was added dropwise, over a period of 6 hours, 1309 g. (11 moles) of purified thionyl chloride, while the temperature was maintained between 10 and 20°. The reaction mixture was stirred for an additional hour and allowed to stand overnight at room temperature. The mixture was then poured into 2.5 liters of ice-water and the benzene layer was separated. The aqueous layer was extracted with four 1-liter portions of ether and the ether extracts were combined with the original benzene layer. The combined organic extracts were washed with a saturated sodium bicarbonate solution, then with cold water and dried over Drierite. The solvents were removed by flash distillation and the residue was fractionated through an 18-inch Vigreux column to yield 640 g. (61%) of colorless 4-chloro-2-butyne-1-ol (IV), b.p. 50° (0.5 mm.), n^{25}_{D} 1.4980, d^{25}_{4} 1.2049; and 184 g. (15%) of 1,4-dichloro-2-butyne, b.p. 70° (20 mm.). IV was a powerful skin irritant.

Anal. Calcd. for C_4H_5ClO: C, 49.96; H, 4.82; Cl, 33.92. Found: C, 49.92; H, 4.64; Cl, 33.96.

4-Bromo-2-butyne-1-ol (V).—A solution of 31 g. (0.30 mole) of sodium bromide and 26 g. (0.25 mole) of 4-chloro-2-butyne-1-ol (IV) in 200 ml. of anhydrous methanol was heated under reflux for 12 hours. The cooled reaction mixture was filtered and the filtrate was concentrated to approximately 100 ml. under reduced pressure. The concentrate was diluted with 400 ml. of cold water. The organic layer was dried over Drierite and distilled through a 6-inch, helix-packed column to yield 22.5 g. (62%) of colorless 4-bromo-2-butyne-1-ol (V), b.p. 46° (0.1 mm.), n^{25}_{D} 1.5200, d^{25}_{4} 1.4742. V also was a strong skin irritant.

Anal. Calcd. for C_4H_5BrO: C, 32.20; H, 3.38; Br, 53.61. Found: C, 32.28; H, 3.41; Br, 53.48.

4-Iodo-2-butyne-1-ol (VI).—To a solution of 165 g. (1.1 moles) of sodium iodide in 600 ml. of anhydrous acetone was added 104.5 g. (1.0 mole) of 4-chloro-2-butyne-1-ol (IV). After the mixture was allowed to stand for 12 hours at room temperature, the sodium chloride was filtered off and the filtrate was concentrated to approximately 200 ml. under reduced pressure. The residue was diluted with 400 ml. of chloroform, and the resulting precipitate was again filtered off. Evaporation of the solvent from the filtrate produced a solid which on recrystallization from a mixture of chloroform and petroleum ether yielded 186 g. (95%) of white leaf-like crystals of 4-iodo-2-butyne-1-ol (VI), m.p. 35.5–36.0°.

Anal. Calcd. for C_4H_5IO: C, 24.50; H, 2.57; I, 64.74. Found: C, 24.35; H, 2.50; I, 64.83.

1-Chloro-4-bromo-2-butyne (VII).—To 209 g. (2.0 moles) of 4-chloro-2-butyne-1-ol (IV) was added dropwise with external cooling over a period of 4 hours, 190 g. (0.68 mole) of freshly distilled phosphorus tribromide in 100 ml. of anhydrous chloroform. After the reaction mixture had been stirred overnight at room temperature, it was diluted with 1 liter of cold water. The chloroform layer was washed with a saturated sodium bicarbonate solution and dried over Drierite. The chloroform was removed by distillation under reduced pressure, and the residue was fractionated through a 12-inch, helix-packed column to yield 235 g. (70%) of 1-chloro-4-bromo-2-butyne (VII), b.p. 45° (2 mm.), n^{25}_{D} 1.5470, d^{25}_{4} 1.6174. The colorless, unpleasant smelling VII was a powerful skin irritant and a lachrymator.

Anal. Calcd. for C_4H_4BrCl: C, 28.68; H, 2.40; halogen, 68.92. Found: C, 28.72; H, 2.31; halogen, 68.80.

1-Chloro-4-iodo-2-butyne (VIII).—To a solution of 49.0 g. (0.250 mole) of 4-iodo-2-butyne-1-ol (VI) in 150 ml. of anhydrous chloroform was added dropwise with external cooling over a 4-hour period a solution of 11.5 g. (0.084 mole) of freshly distilled phosphorus trichloride in 50 ml. of chloroform. After the reaction mixture was stirred overnight at room temperature, it was diluted with 500 ml. of ice-water. The chloroform layer was separated, washed with a saturated sodium carbonate solution and dried over Drierite. The chloroform was removed under reduced pressure in an atmosphere of oxygen-free nitrogen, and the residue was fractionated through a 6-inch, helix-packed column under a nitrogen atmosphere to yield 20 g. (37%) of pale yellow 1-chloro-4-iodo-2-butyne (VIII), b.p. 61° (0.6 mm.), n^{25}_{D} 1.5920, d^{25}_{4} 1.9890. VIII, which was a vesicant and a lachrymator, polymerized rapidly on exposure to air. During one distillation, VIII underwent a violent decomposition.

Anal. Calcd. for C_4H_4ClI: C, 22.40; H, 1.88; halogen, 75.72. Found: C, 21.90; H, 1.83; halogen, 75.61.

1-Bromo-4-iodo-2-butyne (IX).—A cooled solution of 49 g. (0.250 mole) of 4-iodo-2-butyne-1-ol (VI) in 150 ml. of anhydrous chloroform was treated under nitrogen with 22.8 g. (0.084 mole) of freshly distilled phosphorus tribromide in 50 ml. of anhydrous chloroform added dropwise over a period of 4 hours. After the reaction mixture was stirred overnight at room temperature, it was diluted with 500 ml. of ice-water. The chloroform layer was extracted with a saturated sodium bicarbonate solution and dried over Drierite. The solvent was removed under reduced pressure, and the residue was recrystallized from a mixture of chloroform and petroleum ether to yield 58 g. (90%) of highly unstable, very pale yellow needles of 1-bromo-4-iodo-2-butyne (IX), m.p. 20–22°.

Anal. Calcd. for C_4H_4BrI: C, 18.55; H, 1.55; halogen, 79.90. Found: C, 18.38; H, 1.51; halogen, 79.98.

Grignard Reagents of Dihalides.—The Grignard reagents were prepared in a 200-ml. creased flask stirred with a 1700-r.p.m. stirring motor. In agreement with Johnson,[5] it was found that 1,4-dichloro-2-butyne (II) would not form a Grignard reagent. Even when II was entrained with methyl iodide, no appreciable reaction took place. However, both 1-chloro-4-bromo-2-butyne (VII) and 1-chloro-4-iodo-2-butyne (VIII) smoothly formed a Grignard reagent. The presence of a true Grignard reagent and not the elimination of both of the halogens was indicated by the vigorous reaction upon the addition of water. Treatment of an aliquot of the Grignard solution with a solution of Michler ketone, followed by a trace of iodine, gave the characteristic color test.[6]

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Partition Chromatographic Separation of Aromatic Acids[1]

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During the course of work on the metabolism of dibenzanthracene-9,10-C^{14} in mice, purification and resolution of mixtures of radioactive organic aromatic acids was sought through a column partition chromatographic procedure. A survey of the literature[2] indicated that little work[3,4] had been done on the separation of aromatic acids (excepting the naturally occurring aromatic amino acids) using this technique. We have found a

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[8] Analyses were performed by Arthur Tomasewski, Robert Keen and James French. All melting points are corrected.

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[2] See, among others, R. L. M. Synge, *Analyst*, **71**, 256 (1946); F. A. Robinson, *Pharmaceutical J.*, **158**, 46 (1947); T. I. Williams, *Anal. Chim. Acta*, **2**, 635 (1948); H. H. Strain, *Anal. Chem.*, **21**, 75 (1949); **22**, 45 (1950); **23**, 25 (1951); and H. H. Strain, T. R. Sato and J. Engelke, *ibid.*, **26**, 90 (1954).

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[4] S. Gottlieb, THIS JOURNAL, **70**, 423 (1948).