

extracted with hot 1.5 *M* sodium hydroxide and the extract filtered. The clear filtrate was heated almost to boiling and the hot solution acidified with concentrated hydrochloric acid. After cooling, the white product was collected on a Büchner funnel, washed with distilled water and dried *in vacuo* over calcium chloride; weight 9.0 g. (96% yield), m.p. 239–243°. This material can be used without purification for further synthesis. One recrystallization from benzene afforded pure fluorene-1-carboxylic acid, m.p. 245–247°.

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### Preparation and Properties of 3-Chloro-1-iodo-1-propyne and 3-Bromo-1-iodo-1-propyne<sup>1</sup>

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The use of hypohalite ion for the replacement of acetylenic hydrogen atoms in the preparation of 1-haloacetylenes has been reported for the preparation of 1-chloro-1-propyne<sup>2</sup> and 1-bromo-1-propyne.<sup>3</sup> 1,3-Dibromo- and 1-bromo-3-chloro-1-propyne also have been prepared by this method.<sup>3a</sup> The reaction now has been extended to include 3-chloro-1-iodo-1-propyne and 3-bromo-1-iodo-1-propyne.

The only previously reported preparation of 1-iodoacetylenes by the use of hypoiodite ion is that of Blitz and Kupper<sup>4</sup> who prepared diiodo-acetylene by this method. Jacobs and Whitcher<sup>5</sup> used this method in an attempt to prepare iodophenoxyacetylene but obtained triiodophenoxyethylene instead. The formation of the triiodo compound was accounted for by the initial formation of iodo-phenoxyacetylene followed by the addition of iodine to the triple bond. The yields of 3-chloro- and 3-bromo-1-iodo-1-propyne from the corresponding 3-halo-1-propyne and hypoiodite ion in the present work were relatively low because the distillation of the product was not taken to completion. Previous experience with compounds of this type indicated that they might vigorously decompose during the latter part of a distillation.

The compounds were characterized by the usual physical properties, halogen analysis and infrared spectra. There was no indication of an acetylenic-allenic rearrangement which would have been evident by a sharp allene band at 5.1  $\mu$ .<sup>6</sup> The unexplained band near 5.85  $\mu$  found in the spectra of some propargylic halides was also absent in the spectra of 3-chloro- and 3-bromo-1-iodo-1-propyne. Both of the 1-iodo- compounds showed a strong, sharp band at 4.58  $\mu$  ( $\text{—C}\equiv\text{C—}$ ) but no band at 4.65  $\mu$ , the  $\text{—C}\equiv\text{C—}$  stretching band found in the 3-halo-1-propynes.<sup>6</sup> There were also strong bands at 7.05, 7.95, 9.68 and 14.3  $\mu$  for the 3-chloro-1-

iodo-1-propyne and 7.08, 8.35 and 9.65  $\mu$  for the 3-bromo-1-iodo-1-propyne.

The spectra of 3-chloro-, 3-bromo- and 3-iodo-1-propyne also were obtained. The spectra of 3-chloro-1-propyne and 3-bromo-1-propyne failed to show an absorption at 5.10  $\mu$  which would have indicated the presence of halopropadiene from an acetylenic-allenic rearrangement. The spectrum of 3-iodo-1-propyne showed a sharp band at 5.10  $\mu$  and a weak band at 5.85  $\mu$  which confirms the observation of Jacobs and Brill<sup>6</sup> that the iodo compound is actually a mixture of 3-iodo-1-propyne and iodopropadiene. Pauling, Gordy and Saylor<sup>7</sup> have reported that in the 3-halo-1-propynes the carbon-halogen bond distance is longer than normal with the difference being greatest for the carbon-chlorine bond and least for the carbon-iodine bond. They explained this observation by the presence of resonance between the  $\text{H—C}\equiv\text{C—CH}_2\text{X}$  and an ionic structure  $\text{H—}\overset{+}{\text{C}}=\text{C}=\overset{-}{\text{CH}_2}\text{X}$  in addition to the usual ionic structure  $\text{H—C}\equiv\text{C—CH}_2^+\text{X}^-$ . Since both Jacobs and Brill and this work failed to find evidence of the  $\text{CH}_2=\text{C}=\text{CHX}$  structure in the spectra of 3-chloro-1-propyne and 3-bromo-1-propyne it would seem to indicate that the unusually long carbon-chlorine and carbon-bromine bonds did not result from an allene type of structure. Because of the presence of iodopropadiene in the 3-iodo-1-propyne it should follow from Pauling, *et al.*, that the carbon-iodine bond should show the greatest deviation rather than the least, consequently we are unable to correlate our observations with their conclusions.

#### Experimental

**3-Chloro-1-iodo-1-propyne.**—3-Chloro-1-iodo-1-propyne was prepared by the reaction between 3-chloro-1-propyne and hypoiodite ion. The 3-chloro-1-propyne was prepared from propargyl alcohol and phosphorus trichloride (in pyridine).<sup>8</sup> The product obtained had the following physical properties: b.p. 57–59° (751 mm.),  $n_D^{20}$  1.4320; lit.<sup>8</sup> b.p. 56–57°,  $n_D^{20}$  1.4329.

3-Chloro-1-propyne (35 g., 0.5 mole) and 127 g. (0.5 mole) of iodine in 250 ml. of saturated potassium iodide solution were added simultaneously with rapid stirring to a cold aqueous solution (*ca.* 5°) of 224 g. (4.0 moles) of potassium hydroxide over a period of one and a half hours, after which stirring was continued for four hours. The 3-chloro-1-iodo-1-propyne was extracted using diethyl ether and dried over magnesium sulfate.

The 3-chloro-1-iodo-1-propyne was distilled under a nitrogen atmosphere to give 49 g. (49% yield); however, the distillation flask was not taken to dryness because of the danger of violent decomposition. About one-third of the original solution was left in the distillation flask. The product had the following physical properties: b.p. 46.5–47.5° (4 mm.),  $n_D^{20}$  1.5890,  $n_D^{25}$  1.5863,  $n_D^{30}$  1.5836,  $d_4^{20}$  2.1426,  $d_4^{25}$  2.1333,  $d_4^{30}$  2.1249;  $MR(\text{obsd.})$  31.55,  $MR(\text{sum})$  31.72. The compound is unstable and turns dark brown on standing for a few minutes in the atmosphere.

*Anal.* Calcd. for  $\text{C}_3\text{H}_2\text{ClI}$ : Cl, 17.7; I, 63.3. Found: Cl, 17.5; I, 63.6.

**3-Bromo-1-iodo-1-propyne.**—The 3-bromo-1-iodo-1-propyne was prepared by the reaction between 3-bromo-1-propyne and hypoiodite ion.

3-Bromo-1-propyne (119 g., 1.0 mole) (General Aniline and Film Corp.) and 254 g. (1.0 mole) of iodine in 250 ml. of saturated potassium iodide solution were added simultaneously with rapid stirring to a cold aqueous solution (*ca.* 5°) of 224 g. (4.0 moles) of potassium hydroxide. The addition took place over a period of one and a half hours

(7) L. Pauling, W. Gordy and J. H. Saylor, *ibid.*, **64**, 1753 (1942).

(8) L. F. Hatch and V. Chiola, *ibid.*, **73**, 360 (1951).

(1) This research was supported by the United States Air Force under Contract No. AF 18(600)-430. Monitored by Hq., Air Research and Development Command, P. O. Box 1395, Baltimore 3, Md.

(2) A. T. Morse and L. C. Leitch, *Can. J. Chem.*, **32**, 500 (1954).

(3) (a) L. F. Hatch and L. E. Kidwell, *THIS JOURNAL*, **76**, 289 (1954); (b) F. F. Cleveland and J. M. Murray, *J. Chem. Phys.*, **11**, 450 (1943); (c) F. Straus, L. Kollek and W. Heyn, *Ber.*, **63B**, 1868 (1930).

(4) H. Blitz and E. Kupper, *ibid.*, **37**, 4412 (1904).

(5) T. L. Jacobs and W. J. Whitcher, *THIS JOURNAL*, **64**, 2635 (1942).

(6) T. L. Jacobs and W. F. Brill, *ibid.*, **75**, 1314 (1953).

after which stirring was continued for three hours. The 3-bromo-1-iodo-1-propyne was extracted using diethyl ether and dried over magnesium sulfate.

The 3-bromo-1-iodo-1-propyne was distilled under a nitrogen atmosphere to give 77 g. (31% yield); however, about one-third of the original solution was left in the distillation flask. The product had the following physical properties: b.p. 59.5–60.0° (2 mm.),  $n_D^{20}$  1.6435,  $n_D^{25}$  1.6405,  $n_D^{30}$  1.6377,  $d_4^{20}$  2.5663,  $d_4^{25}$  2.5562,  $d_4^{30}$  2.5473;  $MR(\text{obsd.})$  34.53,  $MR(\text{sum})$  34.62. The compound is unstable and turns dark brown on standing for a few minutes in the atmosphere.

*Anal.* Calcd. for  $C_3H_2BrI$ : Br, 32.6; I, 51.8. Found: Br, 32.8; I, 51.9.

**3-Iodo-1-propyne-Iodopropadiene.**—The procedure followed in the preparation of the mixture of 3-iodo-1-propyne and iodopropadiene was that of Jacobs and Brill.<sup>5</sup> The reaction between the 3-bromo-1-propyne and the sodium iodide was carried out in acetone as a solvent and in ethanol. Essentially the same mixture was obtained with either solvent and the 5.85  $\mu$  band was present in the infrared spectrum from the alcohol preparation as well as from the acetone preparation thus eliminating the possibility of carbonyl contamination causing the 5.85  $\mu$  absorption.

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## The Copolymer of Allyl Alcohol and 1,3-Butadiene<sup>1</sup>

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Work in this Laboratory on the relation between polymer composition and the properties of the vulcanized rubber led us to believe that a butadiene-allyl alcohol copolymer might have both good oil resistance and good low temperature properties. Allyl acetate does not polymerize well alone<sup>2</sup> and allyl alcohol is an inhibitor for butadiene polymerization,<sup>3</sup> hence the direct preparation of a copolymer of suitable size did not seem to be feasible.

We have, however, been able to prepare the copolymer in an indirect manner by reducing a butadiene-methyl acrylate copolymer<sup>4</sup> in tetrahydrofuran solution with lithium aluminum hydride.<sup>5</sup> It has been well demonstrated that this reduction will not reduce double bonds which are not conjugated with carbonyl groups.<sup>6</sup> Infrared<sup>7</sup> and elemental<sup>8</sup> analyses of the reduced product indicated that the ester groups in the polymer were completely reduced to primary alcohol groups. This was confirmed by treating the polymer with *p*-nitrophenyl isocyanate to yield a urethan of the correct composition.

(1) The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

(2) P. D. Bartlett and R. Altschul, *THIS JOURNAL*, **67**, 816 (1941); P. D. Bartlett and K. Nozaki, *J. Polymer Sci.*, **3**, 216 (1948).

(3) H. W. Starkweather, P. O. Bare, A. S. Carter, F. B. Hill, V. R. Hurka, C. J. Mighton, P. S. Saunders, H. W. Walker and M. A. Youker, *Ind. Eng. Chem.*, **39**, 210 (1947); P. D. Bartlett and F. A. Tate, *THIS JOURNAL*, **75**, 91 (1953).

(4) A. M. Clifford and J. D. D'Ianni, private communication through the Office of Synthetic Rubber, Dec. 29, 1942.

(5) A. E. Finholt, A. C. Bond and H. I. Schlesinger, *THIS JOURNAL*, **69**, 1199 (1947).

(6) R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 1197 (1947); F. A. Hochstein and W. G. Brown, *ibid.*, **70**, 3484 (1948).

(7) Anderson Physical Laboratory, Champaign, Illinois, carried out the infrared examination of this polymer.

(8) We are indebted to Mr. J. Nemeth and Mrs. L. Chang for the microanalyses.

The butadiene-allyl alcohol copolymer thus obtained was soluble in tetrahydrofuran and could be precipitated by the addition of methanol. The product thus obtained could be dissolved in benzene while it was still wet with methanol. Once the polymer had been allowed to dry, it would not redissolve in benzene even though antioxidants were added to prevent oxidation.

A preliminary evaluation of the oil resistance and low temperature properties of the compounded and vulcanized copolymer was made by Mr. W. K. Taft and Mr. B. G. Labbe of the Government Laboratories at Akron. They found this copolymer to have the best balance between oil resistance at room temperature and low temperature properties that had been observed in this study. More extensive work on the preparation and evaluation of this material will be reported later.

### Experimental

**Butadiene-Methyl Acrylate Copolymer.**—The butadiene-methyl acrylate copolymer was prepared according to the modified mutual GR-S recipe<sup>9</sup> which is listed below. The butadiene used was Phillips Special Purity Research grade. The methyl acrylate was obtained from Rohm and Haas Company and distilled just before use.

The modified mutual GR-S recipe consisted of: water, 34 g.; OSR soap, 1 g.; azo-bis-isobutyronitrile, 0.06 g.; HLM (commercial mixed primary mercaptans of which the main constituent is dodecyl mercaptan), 0.06 g.; methyl acrylate, 3.0 g.; and butadiene, 17.0 g.

In a standard four-ounce screw-cap bottle equipped with a self-sealing rubber gasket were placed 35 g. of soap solution followed by the other constituents in the order indicated. A slight excess of butadiene was added, and this allowed to boil down to the desired weight, sweeping the bottle free of air.

The bottle was then sealed and tumbled end-over-end for 12 hours in a 50° bath. The latices were coagulated with 25 ml. of sodium chloride coagulant using 10 ml. of a 10% solution of phenyl- $\beta$ -naphthylamine as anti-oxidant. The coagulant was a 4% solution of sulfuric acid saturated with sodium chloride. After being washed with distilled water, the polymers were shredded and dried to constant weight in a vacuum desiccator at 1 mm. pressure.

Solubility determinations were made by covering 0.250 g. of dried polymer with 50.0 ml. of dry benzene for 48 hours in a sealed flask, filtering the mixture through a 200-mesh screen and determining the residual solids of an aliquot. Inherent viscosities were determined with the same solution using a modified Ostwald viscometer.

In 12 hours at 50° conversions from 68 to 72% were obtained. These polymers were soluble and had inherent viscosities of 2.5 to 2.8.

*Anal.* Found: C, 85.2; H, 10.6.

**Butadiene-Allyl Alcohol Copolymers.**—Five liters of tetrahydrofuran, which had been refluxed for 24 hours over calcium hydride, was distilled into a 12-l., three-necked, round-bottomed flask equipped with a Soxhlet extractor, a vibro-stirrer,<sup>10</sup> calcium chloride tubes on all openings, and a gas bubbler extended below the surface of the tetrahydrofuran. The flask was then swept out with nitrogen (purified by passing successively through Fieser's solution, concentrated sulfuric acid and finally sodium hydroxide pellets). The nitrogen was allowed to bubble slowly through the reaction during the remainder of the reduction.

A small piece of lithium aluminum hydride (about 1/2 inch in diameter) was placed in the flask to take up any trace of moisture. Thirty grams of butadiene-methyl acrylate copolymer (reprecipitated once from benzene) was dissolved in the tetrahydrofuran with stirring (8–10 hours). Five grams of powdered lithium aluminum hydride was added to the Soxhlet thimble and the reaction mixture was heated

(9) J. W. Wilson and E. S. Pfau, *Ind. Eng. Chem.*, **40**, 530 (1948).

(10) Vibro-Mischer, Model E-1 made by A. G. Für Chemie-Apparatebau, Zurich, Switzerland. Ordinary stirring methods are not satisfactory.