atom and the ligands in these compounds is believed to be through the nitrogen atom, but evidence on this point must await structural studies which are being undertaken in this Laboratory. The unusually high molar ratio found in the compound with formamide, $SiCl_4 \cdot 10HCONH_2$, may be due to the presence of dimeric molecules of the amide.

Experimental

Dried formamide (water content, as determined by titration with Karl Fischer reagent = 0.1%), dried dimethylformamide (water content = 0.01%) and purified-grade (99.8%) silicon tetrachloride were used.

Several samples of each compound were prepared by mixing dilute solutions of the components in anhydrous acetone, ether or benzene as solvents. The addition compound in each case was filtered off, washed well with the solvent, and dried for several days in an Abderhalden drying pistol, under refluxing acetone, at a pressure of 10–15 mm. It was necessary to carry out all transfers of materials in a dry-box in an atmosphere of dry nitrogen to prevent hydrolysis of the addition compounds.

Analyses of the dry compounds are given below. Chlorine was determined by titration of chloride ion with silver nitrate in neutralized aqueous solution. Silicon was determined as silica by ignition after hydrolysis with distilled water. Carbon and hydrogen analyses by combustion were performed by the microanalytical laboratory of the Massachusetts Institute of Technology.

Anal. Calcd. for $SiCl_4 \cdot 10HCONH_2$: C, 19.36; H, 4.88; Cl, 22.86. Found: C, 19.25; H, 5.16; Cl, 22.53, 22.53 (mean = 22.53). Calcd. for $SiCl_4 \cdot 5HCON(CH_3)_2$: C, 33.68; H, 6.59; Si, 5.25; Cl, 26.51. Found: C, 33.61; H, 6.44; Si, 5.29, 4.99 (mean = 5.14); Cl, 26.89, 26.84, 26.87 (mean = 26.87).

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Preparation and Properties of 1-Bromo-1-propyne, 1,3-Dibromopropyne and 1-Bromo-3-chloro-1-propyne[1,2]

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The preparation of 1-bromo-1-propyne by the dehydrobromination of 1,1,2-tribromopropane has been reported[3] but the analysis of the product was sufficiently in error to cast serious doubt upon the purity of the 1-bromo-1-propyne (Calcd. for C_3H_3Br: Br, 67.2. Found: Br, 55.6, 57.7, 56.3). The only other reference to the synthesis of 1-bromo-1-propyne is that of Cleveland and Murray[4] who prepared it by the reaction between propyne and potassium hypobromite.[5] They characterized their product by its boiling point and Raman spectrum.

1,3-Dibromopropyne has been prepared by Lespieau[6] by the dehydrobromination of 1,2,3-tribromopropene.

1-Bromo-1-propyne, 1,3-dibromopropyne and 1-bromo-3-chloro-1-propyne have now been synthesized by the treatment of the appropriate acetylenic compound with an aqueous, alkaline solution of potassium hypobromite. The 1-bromo-1-propyne had a boiling point in agreement with previously reported boiling points but a density different from that given by Loevenich, Losen and Dierichs.[3] It was not possible to obtain an index of refraction because 1-bromo-1-propyne is spontaneously flammable in air. The infrared spectrum of the 1-bromo-1-propyne is in close agreement with the Raman spectrum obtained by Cleveland and Murray.[4] There was no indication of an acetylene–allene rearrangement which would have been evident by a sharp allene band at 5.1 μ.[7]

Both the 1,3-dibromopropyne and the 1-bromo-3-chloro-1-propyne were obtained in good yields with very little rearrangement to the corresponding allene. The spectrum of the dibromide showed a weak band at 5.08 μ indicating the presence of a small amount of dibromopropadiene.

$$\mathrm{Br{-}C{\equiv}C{-}CH_2Br} \rightleftarrows \mathrm{BrHC{=}C{=}CHBr}$$

The same band (5.10 μ) with the 1-bromo-3-chloro-1-propyne was very weak. This decreased tendency for a chloride to undergo rearrangement in the acetylene–allene rearrangement is similar to allylic rearrangement toward which chlorides are more stable than are the bromides.

The unexplained band near 5.85 μ found in the spectra of some propargyl halides was completely absent in the spectra of 1,3-dibromopropyne and 1-bromo-3-chloro-1-propyne. This is similar to the observations of Jacobs and Brill[7] on the spectra of 3-chloro-1-propyne where it was absent and 3-bromo-1-propyne where it was very weak and at 5.7 μ. All three of the 1-bromo compounds showed a strong, sharp —C≡C— band at 4.48 μ, (4.50 μ for 1-bromo-3-chloro-1-propyne) but no band at 4.65 μ, the —C≡C— stretching frequency found in the 3-halopropynes. There was also a strong band at 6.95 μ for 1-bromo-1-propyne, 7.01 μ for 1,3-dibromopropyne and 6.99 μ for 1-bromo-3-chloro-1-propyne.

The usefulness of the hypobromite ion in the preparation of 1-bromo-1-alkynes lies not only in the better yields obtained but also in the mild conditions employed which minimizes rearrangement into the isomeric allene. This same type of reaction was tried using hypochlorite ion with propyne, 3-bromo-1-propyne and 3-chloro-1-propyne but without success.

Experimental

1-Bromo-1-propyne.—The 1-bromo-1-propyne was prepared by the reaction between propyne and hypobromite ion.[4] The hypobromite ion solution was formed by the treatment of 2.68 moles of potassium hydroxide in 1 liter of water at *ca.* 5° with 0.67 mole of bromine. The propyne (Research Grade, Farchan Research Laboratories) was slowly passed through this cold solution until all of the hypobromite ion had reacted. The 1-bromo-1-propyne was extracted using diethyl ether and dried over magnesium sulfate.

The 1-bromo-1-propyne was distilled under an atmosphere of nitrogen to give a 75% yield based on the hypobromite ion; b.p. 64–65° (750 mm.), d^{20}_{4} 1.5325, d^{25}_{4} 1.5222, d^{30}_{4} 1.5122; lit.[3] b.p. 65°, n^{25}_{D} 1.44482, d^{25}_{0} 1.35015.

Anal. Calcd. for C_3H_3Br: Br, 67.2. Found: Br, 67.2, 67.1.

1,3-Dibromopropyne.—The 1,3-dibromopropyne was prepared by the treatment of 0.67 mole of 3-bromo-1-propyne

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(2) Monitored by Hq., Air Research and Development Command, P. O. Box 1395, Baltimore 3, Md.

(3) J. Loevenich, J. Losen and A. Dierichs, *Ber.*, **60B**, 950 (1927).

(4) F. F. Cleveland and J. M. Murray, *J. Chem. Phys.*, **11**, 450 (1943).

(5) F. Straus, L. Kollek and W. Heyn, *Ber.*, **63B**, 1868 (1930).

(6) R. Lespieau, *Ann. chim.*, [7] **11**, 269 (1897).

(7) T. L. Jacobs and W. F. Brill, THIS JOURNAL, **75**, 1314 (1953).

(propargyl bromide) with 0.67 mole of hypobromite ion in a manner similar to that used for 1-bromo-1-propyne. The 3-bromo-1-propyne was obtained by the reaction between propargyl alcohol (General Aniline and Film Corp.) and phosphorus tribromide in the presence of pyridine[8] (b.p. 36–37° (130 mm.), n^{20}_{D} 1.4917; lit.[7] b.p. 46° (200 mm.), n^{20}_{D} 1.4929). The 1,3-dibromopropyne was obtained in a 45% yield and had the following properties: b.p. 53–54° (10 mm.), n^{20}_{D} 1.5690, n^{25}_{D} 1.5664, n^{30}_{D} 1.5633, d^{20}_{4} 2.1894, d^{25}_{4} 2.1785, d^{30}_{4} 2.1676; lit.[6] b.p. 52–55° (10 mm.). It was not spontaneously flammable in air.

Anal. Calcd. for $C_3H_2Br_2$: Br, 80.7. Found: Br, 80.6, 80.6.

1-Bromo-3-chloro-1-propyne.—1-Bromo-3-chloro-1-propyne was prepared by the addition of 0.34 mole of 3-chloro-1-propyne (propargyl chloride) to a cold, alkaline solution containing 0.34 mole of hypobromite ion. The 3-chloro-1-propyne was made from propargyl alcohol and phosphorus trichloride (in pyridine) in a manner similar to that used in the preparation of 3-bromo-1-propyne.[8] The 3-chloro-1-propyne had the following physical properties: b.p. 57–58° (746 mm.), n^{20}_{D} 1.4338; lit.[7] b.p. 56°, n^{20}_{D} 1.4344. A 53% yield of 1-bromo-3-chloro-1-propyne was obtained. The 1-bromo-3-chloro-1-propyne had the following physical properties: b.p. 47–48° (30 mm.), n^{20}_{D} 1.5207, n^{25}_{D} 1.5184, n^{30}_{D} 1.5158, d^{20}_{4} 1.7598, d^{25}_{4} 1.7519, d^{30}_{4} 1.7433. It was not spontaneously flammable in air.

Anal. Calcd. for C_3H_2BrCl: Br, 52.1; Cl, 23.1. Found: Br, 51.9; Cl, 22.4.

Infrared Spectra.—The infrared spectrum of 1-bromo-1-propyne was obtained through the courtesy of Robert E. Kitson and E. I. du Pont de Nemours and Co., Wilmington, Del. A Perkin-Elmer Model C21 spectrophotometer was used with sodium chloride optics and a cell thickness of 0.032 mm.

The spectra of 1,3-dibromopropyne and 1-bromo-3-chloro-1-propyne were obtained through the courtesy of William F. Hamner and Monsanto Chemical Company, Texas City, Texas. A Baird Associates double-beam recording infrared spectrophotometer was used with sodium chloride optics and a cell thickness of 0.099 mm.

Following are the principal wave lengths in microns (w = weak, m = medium, s = strong).

1-Bromo-1-propyne.—3.00m, 3.35s, 3.40m, 3.49s, 3.65w, 4.48m, 4.87w, 6.95s, 7.33w, 7.95m, 9.15m, 9.75s.

1,3-Dibromopropyne.—3.26m, 3.33m, 3.51w, 3.66m, 4.40s, 4.48s, 4.70m, 5.08w, 7.01s, 8.28s, 8.70m, 9.27s, 11.25m, 11.60m, 12.63s, 13.02s, 15.12m.

1-Bromo-3-chloro-1-propyne.—3.19w, 3.37w, 4.50s, 5.10vw, 6.99m, 7.92s, 8.54w, 9.49s, 11.08w, 14.29s.

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An Improved Procedure for the Deamination of 5-Aminotetrazole

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Tetrazole can be made on a small scale in the laboratory by the reaction of hydrogen cyanide and hydrazoic acid,[1–4] but this direct synthesis is both time consuming and somewhat hazardous for the preparation of large quantities. At the same time most of the indirect methods (reviewed in ref. 3) are also unsuitable because of the unavailability of the starting materials. On the other hand, 5-aminotetrazole is commercially available[5] and its conversion to tetrazole in a practical manner would be attractive. However, the procedures reported for this conversion: namely, the reduction of 5-tetrazolediazonium chloride with stannous chloride[6] or with hypophosphorous acid,[7] or the reduction of sodium 5-tetrazolediazonium hydroxide with alcohol in the presence of carbon dioxide,[6] possess the disadvantage that dilute solutions are employed and the isolation of the product is troublesome. The extreme explosiveness of tetrazolediazonium salts[8,9] in aqueous solutions exceeding about 2% concentration necessitates the use of such dilute solutions.

Since the reduction of tetrazolediazonium chloride by hypophosphorous acid is exceedingly rapid even at 0°, a method was suggested that eliminated both the shortcomings of the dilute solution and the danger of explosion. This method involves the diazotization of 5-aminotetrazole in the presence of hypophosphorous acid (no other acid is needed) so that the diazonium salt is reduced almost as rapidly as it is formed. No large concentration of diazonium salt can ever exist and consequently more concentrated solutions can be used throughout. From a detailed investigation of the reaction variables a method has been developed which consistently gives 85–95% yields of crude product, melting 140–150°, on a scale as large as ten moles. The yields of purified compound, melting at 153–155°, vary from 75–80%. Initial concentrations of 5-aminotetrazole as high as 15% have been employed without difficulty. By operating at 35–45°, instead of 0–5°, the time for complete reaction prior to isolation of the tetrazole can be reduced to less than one hour without loss in product yield or quality. In fact, somewhat better yields are probably obtained by working at the higher temperatures. In addition, smaller amounts of by-products are formed since the rapid reduction of the diazonium salt apparently takes precedent over competing solvolytic reactions. This is probably the main reason why the conversions to tetrazole by this method are much better than those obtained in procedures where all of the 5-aminotetrazole is diazotized prior to reduction. In several experiments by the latter method, the yields of impure tetrazole were less than 50% and substantial amounts of other compounds were isolated.

The applicability of this idea of diazotizing an amino compound in the presence of hypophosphorous acid was further examined to a limited extent. 3-Amino-1,2,4-triazole behaves like the aminotetrazole in that both the diazotization and reduction are rapid. The yields of purified 1,2,4-triazole approach 70%. Anilines with electronegative substituents in the 2-position also show promise of giving fairly satisfactory results by this procedure (Table I) although more examples will have to be collected before a general conclusion can be made. On the other hand, anilines with substituents in the 4-position are not cleanly or smoothly deaminated under these conditions. In addition, with 1- or 2-naphthylamine the yields of naphthalene are very poor (less than 10%) and much coupling to form diazoamino compounds occurs; the reduction of

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