

(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 pyridine⁸ (b.p. 36–37° (130 mm.), n_D^{20} 1.4917; lit.⁷ b.p. 46° (200 mm.), n_D^{20} 1.4929). The 1,3-dibromopropyne was obtained in a 45% yield and had the following properties: b.p. 53–54° (10 mm.), n_D^{20} 1.5690, n_D^{25} 1.5664, n_D^{30} 1.5633, d_4^{20} 2.1894, d_4^{25} 2.1785, d_4^{30} 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_D^{20} 1.4338; lit.⁷ b.p. 56°, n_D^{20} 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_D^{20} 1.5207, n_D^{25} 1.5184, n_D^{30} 1.5158, d_4^{20} 1.7598, d_4^{25} 1.7519, d_4^{30} 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.

(8) A. Kirmann, *Bull. soc. chim.*, [4] **39**, 698 (1926).

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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 available⁵ 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 chloride⁶ or with hypophosphorous acid,⁷ or the reduction of sodium 5-tetrazolediazonium hydroxide with alcohol in the presence of carbon dioxide,⁸ 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

(1) O. Dimroth and G. Fester, *Ber.*, **43**, 2219 (1910).

(2) H. Rathsburg, British Patent 185,555 (1921).

(3) F. R. Benson, *Chem. Revs.*, **41**, 17 (1947), footnote 1.

(4) J. S. Mehina and R. M. Herbst, *J. Org. Chem.*, **15**, 1088 (1950).

(5) Fairmount Chemical Co., Newark, New Jersey.

(6) J. Thiele and H. Ingle, *Ann.*, **287**, 233 (1895).

(7) R. Stolle, *Ber.*, **62**, 1118 (1929).

(8) J. Thiele, *Ann.*, **270**, 54 (1892).

(9) J. Thiele and J. T. Marais, *ibid.*, **278**, 144 (1893).

the diazonium salt (as judged by the rate of gas evolution) is apparently slow.

Experimental

Tetrazole by the Deamination of 5-Aminotetrazole.—A solution of 69.0 g. (1.0 mole) of sodium nitrite in 200 ml. of water was added with vigorous agitation to a slurry consisting of 103.0 g. (1.0 mole) of 5-aminotetrazole monohydrate, 145 g. (1.1 moles) of 50% hypophosphorous acid and 500 ml. of water in a 1500 ml. beaker. The temperature was first allowed to rise to about 35°, after which it was maintained in the range 33–36° by external cooling with an ice-water-bath; the time required for the addition of the nitrite was 25 to 30 minutes. The cooling bath was finally replaced by a water-bath at 35° and the stirring continued for 30 minutes more in order to complete the reaction. The pale-yellow colored solution was cooled to 25°, adjusted to pH 3.4–3.6 (pH meter) with 50% sodium hydroxide solution, and vacuum evaporated on the steam-bath at water-pump pressure to incipient crystallization. The somewhat sirupy residue was refluxed for 10–15 minutes with 500 ml. of 50–50 acetone-ethanol, after which the supernatant liquid was decanted from the insoluble gum. This extraction by refluxing and decanting was repeated with one 250-ml. portion, and four 100-ml. portions of the same mixed solvent. The combined extracts were evaporated to dryness on the steam-bath and the residue of very impure tetrazole was re-extracted with the following portions of boiling ethyl acetate: one 375 ml., one 125 ml. and four 60 ml. Any insoluble gum was discarded. Evaporation of the combined ethyl acetate solutions yielded 65 g. (92.6%) of tetrazole melting at 140–150°. The crude tetrazole was dissolved in 125 ml. of hot glacial acetic acid, cooled to 15°, and filtered. The crystalline product was washed with 25 ml. of cold acetic acid and then with two 50-ml. portions of diethyl ether. The yield of dried product was 43.3 g., m.p. 156–158° (cor.); Mehina and Herbst⁴ reported 157.5–158°. By evaporating the combined mother liquors and washings to 65 ml., cooling, filtering and washing with cold diethyl ether-acetic acid (2:1), there was recovered 11.0 g. more of tetrazole, melting 156–158°. The total recovery amounted to 54.3 g., or 77.6% based on the 5-aminotetrazole.

Anal. Calcd. for CH₂N₄: eq. wt., 70.06. Found: eq. wt., 70.9.

In the remaining acetic acid recrystallization mother liquors there is some kind of phosphorus-containing compound but it was never isolated in pure form for identification and analyses.

Tetrazole and Sodium 5-Chlorotetrazole.—A slurry consisting of 19.4 g. (0.188 mole) of 5-aminotetrazole monohydrate, 80 ml. of 20% sodium hydroxide solution, 56.8 ml. of 20% sodium nitrite solution and 120 g. of crushed ice was added all at once with stirring to a freshly prepared slurry of crushed ice (400 g.), concentrated hydrochloric acid (68 ml.) and 200 ml. of cold H₂O. The temperature held at –2.5 to –3°. After the mixture had been stirred for ten minutes, 28 g. (0.215 mole) of 50% hypophosphorous acid was added. Evolution of gas began immediately. During the two hours allowed for the reduction of the diazonium compound, the temperature was gradually raised to 20°. The solution was adjusted to pH 2.5 with sodium hydroxide solution and then evaporated to dryness under reduced pressure. The residue was extracted with one 200-ml. and four 50-ml. portions of boiling 50–50 ethanol-acetone mixture. Evaporation of the combined extracts left 26.5 g. of material. When the latter was extracted with one 100-ml. and four 50-ml. portions of hot ethyl acetate and the extracts evaporated, there was recovered 5.6 g. (42.6%) of crude tetrazole, m.p. 148–156°, softening 130–135°. In duplicate experiments the yields varied from 26 to 46%.

The ethyl acetate insoluble material was dissolved in 35 ml. of hot water, filtered and allowed to cool slowly. There was recovered 5.4 g. (18.7%) of sodium 5-chlorotetrazole, as the 1.5 hydrate, which decomposed explosively at about 253–255° (depends on the heating rate).

Anal. Calcd. for CN₄ClNa·1.5 H₂O: C, 7.82; H, 1.97; N, 36.49; Cl, 23.10; Na, 14.98. Found: C, 7.92; H, 2.03; N, 36.56; Cl, 22.39; Na, 14.07.

5-Chlorotetrazole was isolated from its sodium salt by precipitation as the copper salt and treatment of the latter

with hydrogen sulfide. The unpurified chlorotetrazole melted at 72–73°, Stolle reported 73°; the measured equivalent weight was 105.7 versus the theoretical 104.51.

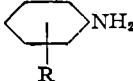
Evaporation of the aqueous mother liquors, from which the sodium 5-chlorotetrazole had been removed, left a material which was almost completely soluble in absolute ethanol and which contained phosphorus, but which even after repeated recrystallization, could not be obtained in a sufficiently pure state for satisfactory and meaningful analyses.

Triazole by the Deamination of 3-Amino-1,2,4-triazole.—A solution of 35.0 g. (0.5 mole) of sodium nitrite in 100 ml. of water was added with agitation during 30 minutes to a solution consisting of 42.0 g. (0.5 mole) of 3-amino-1,2,4-triazole, 72.5 g. (0.55 mole) of 50% hypophosphorous acid, 40 ml. of concentrated hydrochloric acid and 250 ml. of water. The temperature was maintained at 35–38°. There was a steady evolution of gas during this period. After the reaction mixture had stood for an additional 30 minutes at 35°, the pH was adjusted to neutral with a 50% solution of sodium hydroxide. The solution was then evaporated to dryness under reduced pressure and the residue extracted with seven 100-ml. portions of boiling ethyl acetate. Evaporation of the ethyl acetate left 26.0 g. (75.3%) of crude 1,2,4-triazole, m.p. 110–120°. The product was best purified by vacuum distillation, followed by one recrystallization from ethyl acetate; long white needles, m.p. 120.5–121° (Pellizzari and Cuneo¹⁰ reported 121°).

Deamination of Substituted Anilines.—A slurry consisting of 0.1 mole of the aniline, 17.0 ml. of concentrated hydrochloric acid and 100 ml. of water was heated to boiling, cooled rapidly to 35° with stirring, treated first with 14.5 g. of 50% hypophosphorous acid, and then during 30 minutes with 6.9 g. (0.1 mole) of sodium nitrite in 20 ml. of water. The temperature was maintained at 30–35°. After one more hour the gas evolution had ceased and the solution no longer gave a positive nitrite test. If the product was volatile in steam, the reaction mixture was adjusted to pH 9–10 with a 50% solution of sodium hydroxide and steam distilled. The distillate was then acidified and steam distilled again. The product was separated from the distillate by conventional means. The benzoic acid which resulted from the deamination of the aminobenzoic acids was filtered from the acid reaction mixture after the latter had been cooled overnight at 5°. The crude product was recrystallized from water. Results are summarized in Table I.

TABLE I

DEAMINATION OF SUBSTITUTED ANILINES

R					
	2-NO ₂	4-NO ₂	2-COOH	4-COOH	4-C ₆ H ₅
Yield of					
C ₆ H ₅ , %	79	17	64 ^a	31 ^b	33 ^c

^a The melting point of this once recrystallized material was 116–119°, eq. wt. 124.3 (theory 122.1). ^b The melting point of this once recrystallized material was 110–118°, eq. wt. 124.6. ^c The melting point was 68.5–69.5° (reported, 69–70° for diphenyl).

(10) G. Pellizzari and G. Cuneo, *Gazz. chim. ital.*, **24**, I, 510 (1894).

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The Solubility of Potassium Chromate in Aqueous Ethanol Solutions at 25°

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Ethanol-water solutions were prepared by measuring appropriate amounts of each liquid with calibrated burets (or pipets). The solvent compositions were thus known to at least one part per thousand. C.P. K₂CrO₄ was added, and the mixtures were stirred by rotating them in a water-