2,4-Diaminotrihalopropyltriazines Derived from γ-Trihalobutyronitriles

Leon H. Chance* and Judy D. Timpa
Southern Regional Research Center,[†] *New Orleans, Louisiana 70179*

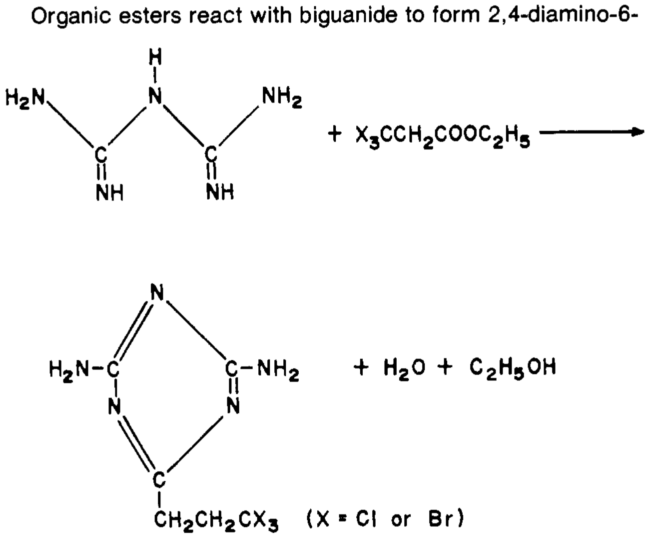
γ-Trichlorobutyronitrile and γ-tribromobutyronitrile were prepared in improved yields by modifications of reported methods of reacting the appropriate haloform with acrylonitrile. Methyl γ-trichlorobutyrate, ethyl γ-trichlorobutyrate, methyl γ-tribromobutyrate, and ethyl γ-tribromobutyrate were prepared from the corresponding nitriles. 2,4-Diamino-6-(3,3,3-trichloro-1-propyl)-1,3,5-triazine and 2,4-diamino-6-(3,3,3-tribromo-1-propyl)-1,3,5-triazine were prepared by the reaction of the corresponding methyl or ethyl trihalobutyrates with biguanide. The tetramethylol derivatives of the triazines, viz., 2,4-bis[di(hydroxymethyl)amino]-6-(3,3,3-trichloro-1-propyl)-1,3,5-triazine and 2,4-bis[di(hydroxymethyl)amino]-6-(3,3,3-tribromo-1-propyl)-1,3,5-triazine, were prepared by the reaction of the triazines with alkaline aqueous formaldehyde.

In the course of investigating flame retardants for cotton textiles, we were interested in preparing halogenated triazines.

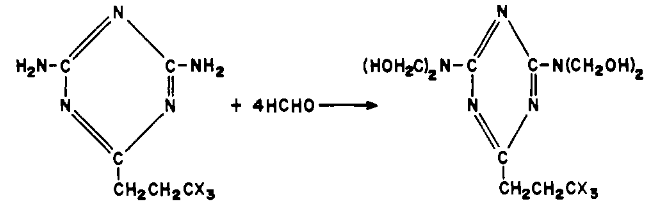
Bruson et al. (*1*) prepared γ-trichlorobutyronitrile (TCBN) and γ-tribromobutyronitrile (TBBN) in yields of only 12 and 5%, respectively, by the reaction of the corresponding haloform with acrylonitrile in the presence of strongly basic catalysts such as finely powdered potassium hydroxide or aqueous 40% trimethylbenzylammonium hydroxide. We modified the procedure and prepared TCBN and TBBN in improved yields by using 10 N aqueous KOH as the catalyst and acetonitrile as a solvent to bring the catalyst into better contact with the reactants. By this method, TCBN and TBBN were obtained in yields of 18 and 41%, respectively.

Methyl γ-trichlorobutyrate, ethyl γ-trichlorobutyrate, methyl γ-tribromobutyrate, and ethyl γ-tribromobutyrate, all new compounds, were obtained in yields of 45, 90, 85, and 99%, respectively, by the reaction of TCBN and TBBN with water and methyl or ethyl alcohol in the presence of dry hydrogen chloride catalyst.

Organic esters react with biguanide to form 2,4-diamino-6-alkyltriazines (or guanamines) (*2, 3*). We prepared two new compounds, 2,4-diamino-6-(3,3,3-trichloro-1-propyl)-1,3,5-triazine (DACPT) and 2,4-diamino-6-(3,3,3-tribromo-1-propyl)-1,3,5-triazine (DABPT), by the reaction of biguanide with the corresponding methyl or ethyl γ-trihalobutyrates at room temperature in methanol solvent. Fresh biguanide was prepared by refluxing anhydrous biguanide sulfate in a methanol solution of sodium methylate (*4*). The preparation of the triazines is represented by the following equation:



Finally, we prepared the tetramethylol derivatives of DACPT and DABPT, viz., 2,4-bis[di(hydroxymethyl)amino]-6-(3,3,3-trichloro-1-propyl)-1,3,5-triazine and 2,4-bis[di(hydroxymethyl)amino]-6-(3,3,3-tribromo-1-propyl)-1,3,5-triazine, by the reaction of DACPT and DABPT with alkaline aqueous formaldehyde. They were obtained as pure white crystalline compounds. No references to pure crystalline methylol derivatives of 2,4-diamino-6-haloalkyltriazines could be found. The equation for the reaction is represented by the following equation:



(X = Cl or Br)

The tetramethylol derivative of DABPT was found to be an excellent flame retardant for cotton textiles when polymerized on cotton fabrics. This research will be published as a separate paper.

Experimental Section

Melting points were determined in capillary tubes and are uncorrected. Elemental analyses (C, H, N, Br) were performed and were submitted for review by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra of samples in KBr disks were obtained with a Perkin-Elmer Model 621 spectrometer.

γ-Trichlorobutyronitrile (TCBN). Chloroform (186.0 g, 1.56 mol) was placed in a flask equipped with a mechanical stirrer, air condenser, and dropping funnel. The chloroform was cooled to 2 °C by placing the flask in a cooling bath. Aqueous 10 N KOH (90 ml) was cooled to 2 °C and added, with stirring, to the chloroform. Cooling is important to prevent a reaction at this point. Acetonitrile (150 ml) was cooled to 0–5 °C and added to the mixture, followed by acrylonitrile (81.0 g, 1.53 mol), also previously cooled to 0–5 °C. The mixture was stirred for 4 h while maintaining the temperature at 0–5 °C. The mixture was washed with two 75-ml portions of water. The water layer in the second portion was adjusted to pH 6.7–7.0 with dilute HCl. The top water layers were discarded. The bottom layer was separated and the unreacted materials were recovered by distillation at 61–84 °C. The residual oil was vacuum distilled. A yield of 47.0 g (18% of the theoretical yield) of γ-trichlorobutyronitrile was obtained, which solidified to a white crystalline solid (mp 35.5–40.5 °C) in the receiver. After recrystallization from methanol the melting point was 39–40 °C (lit. mp 41 °C). TCBN sublimes at room temperature; crystals placed on a watch glass disappear on standing overnight.

γ-Tribromobutyronitrile (TBBN). Bromoform (759 g, 3.0 mol)

[†] One of the facilities of the Southern Region, Agricultural Research Service, U.S. Department of Agriculture.

was placed in a 2 l., four-neck flask equipped with a mechanical stirrer, dropping funnel, immersion thermometer, and air condenser. The flask was immersed in a cooling bath, and the bromoform was cooled to about 5 °C. Acetonitrile (300 ml) was added and the mixture was again cooled to 5 °C. Acrylonitrile (159.2 g, 3.0 mol) was added and the mixture was cooled to 3–5 °C. KOH (10 N, 180.0 g) was added in 9-ml portions every 15 min over a 5-h period, maintaining the temperature below 10 °C. The temperature was then maintained at 10 °C or less for an additional 1.5 h. The mixture was stirred overnight at a water bath temperature of 25 °C (room temperature). The total reaction time was about 23 h. The reaction mixture turned black soon after the addition of KOH was begun. The solvent (acetonitrile) and unreacted bromoform and acrylonitrile were removed by vacuum distillation on a rotary evaporator. The black residue was slurried with 1500 ml of water. The pH of the slurry was 10.3. It was adjusted to pH 7.0 by adding about 4.0 g of concentrated HCl. The slurry was filtered and the black solid was washed with water and dried at 65 °C. The solid was refluxed in 1800 ml of absolute ethanol for 25 min and filtered while hot. An insoluble black powder (37 g) remained on the filter. The filtrate was refluxed with carbon black, filtered, and cooled to allow crystallization. A yield of 372.0 g of white crystals was obtained. A second crop of crystals weighing 6.2 g was obtained by concentrating the filtrate to a volume of 450 ml. The total yield of γ-tribromobutyronitrile, mp 95.5–98 °C, was 378.2 g (41% based on acrylonitrile). A sample recrystallized from ethanol had a mp of 96–98 °C (lit. mp 98 °C). The black powder was not identified.

A typical procedure for the preparation of ethyl γ-tribromobutyrate is given below. The same procedure was used to prepare methyl γ-tribromobutyrate and methyl and ethyl γ-trichlorobutyrate, using the appropriate nitrile and alcohol.

Ethyl γ-Tribromobutyrate. TBBN (137.8 g, 0.45 mol), water (8.1 g, 0.45 mol), and absolute ethanol (250 ml) were placed in a flask equipped with a mechanical stirrer, reflux condenser, and gas inlet tube. Hydrogen chloride was bubbled into the mixture at a rapid rate. The mixture warmed spontaneously, and most of the TBBN dissolved within 7–8 min. Within 10–15 min the mixture began to reflux spontaneously and NH_4Cl started to precipitate. HCl addition was continued for a total of 2.25 h. After standing overnight at room temperature, the reaction mixture was slowly heated to reflux, allowed to cool slowly to room temperature, and then cooled in an ice water bath. The NH_4Cl was removed by filtration and the ethanol was removed from the filtrate on a rotary evaporator. A pale yellow oil that contained a small amount of NH_4Cl was obtained. The oil was dissolved in benzene (100 ml) and filtered to remove the NH_4Cl. The benzene filtrate was shaken in a separatory funnel with 100 ml of water containing 5 g of Na_2CO_3. The benzene layer was separated and washed again with 100 ml of water. The benzene solution was dried over anhydrous Na_2SO_4 and the benzene removed on a rotary evaporator. The residual oil was distilled under vacuum to yield 147.5 g (93%) of ethyl γ-tribromobutyrate, a clear colorless liquid boiling at 73 °C (0.13 mm). The IR spectrum showed absorption bands at 1735 (s, C=O) and 608 (m, C—Br) cm^{-1}.

Methyl γ-Tribromobutyrate. A clear colorless liquid boiling at 78 °C (0.16 mm) was obtained in a yield of 85%. Upon cooling, it crystallized to a white solid, mp 39–40 °C. The IR spectrum showed absorption bands at 1735 (s, C=O) and 605 (m, C—Br) cm^{-1}.

Ethyl γ-Trichlorobutyrate. A clear colorless liquid boiling at 74 °C (0.13 mm) was obtained in a yield of 90%. The IR spectrum showed absorption bands at 1735 (s, C=O) and 790(m, C—Cl) cm^{-1}.

Methyl γ-Trichlorobutyrate. A clear colorless liquid boiling at 57–58 °C (0.14 mm) was obtained in a yield of 45%. The IR spectrum showed absorption bands at 1735 (s, C=O) and 780 (m, C—Cl) cm^{-1}.

2,4-Diamino-6-(3,3,3-tribromo-1-propyl)-1,3,5-triazine (DABPT). Absolute methanol (1300 ml) was placed in a three-neck flask equipped with a mechanical stirrer, a stopper, and a reflux condenser topped with a soda-lime trap to exclude CO_2. Metallic sodium (28.3 g, 1.23 g-atoms) was added gradually in small pieces to the methanol. Biguanide sulfate dihydrate was dried at 110 °C to remove the water of crystallization. Anhydrous biguanide sulfate (184.7 g, 0.61 mol) was added to the methanol solution of sodium methylate. The mixture was refluxed for 3 h, with stirring, and then cooled to room temperature. It was not necessary to filter off the Na_2SO_4 before proceeding to the next step. Ethyl γ-tribromobutyrate (434.7 g, 1.23 mol) was added in a small stream over a 20-min period. Stirring was continued overnight at room temperature (26–27 °C) for 18 h. The white precipitate was filtered, washed with fresh methanol, and dried in an oven at 70–85 °C. The precipitate, consisting of a mixture of DABPT and Na_2SO_4, was stirred with 725 ml of water to dissolve the Na_2SO_4. The insoluble DABPT was filtered, washed with 500 ml of water, and finally washed with 125 ml of cold methanol and dried at 65 °C. The yield was 304.6 g (63.5%), mp 170–71 °C.

A 51% yield of DABPT was obtained when methyl γ-tribromobutyrate was used in the reaction with biguanide. The IR spectrum showed absorption bands at 1622 (s, NH), 1648 (m, NH), and 601 (s, C—Br) cm^{-1}. Several bands appeared at 3000–3500 cm^{-1} (probably NH).

2,4-Diamino-6-(3,3,3-trichloro-1-propyl)-1,3,5-triazine (DACPT). DACPT was prepared by the same procedure as that used for DABPT. The yield of white crystals was 62%, mp 187–88 °C. The IR spectrum showed absorption bands at 1616 (s, NH), 1635 (w, NH), and 785 (m, C—Cl) cm^{-1}. Several bands appeared at 3100–3500 cm^{-1} (probably NH).

2,4-Bis[di(hydroxymethyl)amino]-6-(3,3,3-tribromo-1-propyl)-1,3,5-triazine. DABPT (95.52 g, 0.24 mol) and 37% aqueous formaldehyde (285.5 g, 3.55 mol) were placed in a flask and adjusted to pH 10.0 by adding 2.0 g of 20% NaOH. The mixture was stirred at room temperature for 7 h. The DABPT completely dissolved in 6–6.5 h. The clear solution, after standing overnight, was added in a slow stream to 700 ml of water, with stirring, at room temperature. The tetramethylol derivative separated as a white powder. It was cooled to about 10 °C, filtered, washed on the filter with 200 ml of ice water, and dried at room temperature. The yield was 116.8 g (93%), mp 116–17 °C dec. The IR spectrum showed absorption bands at 3380 (s, OH) and 600 (s, C—Br) cm^{-1}. All of the bands attributed to NH for DABPT disappeared for methylolated DABPT.

2,4-Bis[di(hydroxymethyl)amino]-6-(3,3,3-trichloro-1-propyl)-1,3,5-triazine. The tetramethylol derivative of DACPT was prepared by the same procedure as that used for DABPT. The yield of white crystals was 61%, mp 100–102 °C. The IR spectrum showed absorption bands at 3370 (s, OH) and 790 (m, C—Cl). All of the bands attributed to NH for DACPT disappeared for methylolated DACPT.

Acknowledgments

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