pounds are thermally stable, are relatively insensitive to impact, and possess a wide liquid range.

Experimental Section

General Procedures. **Caution!** Most of the products and starting materials described are explosives of moderate to considerate sensitivity to initiation by impact, shock, friction, and other means and should be handled with care.

Melting points are uncorrected. Isolation and purification were accomplished by liquid chromatography for safety reasons. Infrared analyses were carried out with a Perkin-Elmer 137 infrared spectrophotometer. Gas-chromatographic analyses were carried out on an F&M 700 instrument using a 10 ft × 3/16 in. stainless-steel column packed with 3% QF-1 on 40/80 mesh Chromosorb T.

Final structure proof was obtained in every case with complete elemental analyses.

Polyalkylene Glycol Diazides. The preparation of polyethylene glycol 400 diazide (PEG-400-DA) is given as typical of this class of compounds. A mixture of 35 mL of 98% nitric acid, 30 mL of 96% sulfuric acid, and 100 mL of methylene chloride was cooled to 0–5 °C, and 40 g (0.1 mol) of polyethylene glycol 400 was added dropwise in 20 min, the temperature being maintained at 5–10 °C by external cooling. The reaction mixture was stirred 1 h and poured onto ice. The methylene chloride layer was separated, washed successively with water, sodium bicarbonate solution, and water, dried over magnesium sulfate, passed over a neutral alumina column, and concentrated to give 42.1 g (86%) of colorless oil.

A mixture of 9.8 g (0.02 mol of polyethylene glycol 400 dinitrate, 5.2 g (0.08 mol) of sodium azide, 40 mL of dimethylformamide, and 10 mL of water was heated with stirring at 90 °C for 24 h. The mixture was cooled, diluted with 100 mL of methylene chloride, and washed with 3 × 100 mL of water. The methylene chloride solution was concentrated to give 8.4 g (100%) of light yellow liquid, n^{23}_D 1.4713. The product was dissolved in chloroform, passed through an alumina column, and concentrated to give a quantitative recovery of a colorless liquid. The infrared spectrum showed a strong absorption for N_3 at 4.7 μm and no characteristic absorption for the ONO_2 group.

Tetraazido Polyesters. The preparation of bis(2,3-diazidopropyl) adipate (2,3-DAPA) is given as typical of this class of compounds. 2,3-Diazidopropanol (8.52 g, 0.06 mol) in 20 mL of dry carbon tetrachloride was added dropwise to 5.49 g (0.03 mol) of adipyl chloride in 30 mL of dry carbon tetrachloride while the temperature was held below 20 °C. At the end of the addition, the cooling bath was removed and the temperature was allowed to rise to 25 °C. The reaction mixture was allowed to stir at ambient temperature for 18 h under a slow flow of nitrogen to purge HCl produced in the reaction. At the end of this period, the reaction mixture was washed with water, dilute bicarbonate solution, and a final water wash. The resultant colorless solution was stripped of solvent to yield 9.8 g (83%) of colorless oil.

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Basicities of Selected Quinoxalines

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The basicities of a series of quinoxalines were determined by potentiometric titration.

As part of a continuing investigation of the relationship between the structure and physical properties of nitrogen heterocyclic systems, we were interested in the basicities of selected quinoxalines and the hyperfine splitting patterns for the corresponding anion radicals. For this study the pK_a values were needed for the conjugate acids of 2,3,6,7-tetramethylquinoxaline (**1**) and dibenzo[*f*,*h*]quinoxaline (**5**). Accordingly, the basicities were determined by potentiometric titration (*1*) for the series of quinoxalines reported in Table I. This method has been used in related studies (*2–4*), and it has been established that half-neutralization potentials (HNPs) and apparent acid dissociation constants (pK_a) are linearly related (*5*).

Table I. Basicity Data for Quinoxalines

	compd	HNP, mV	pK_a	ref
1	2,3,6,7-tetramethylquinoxaline	417	2.12	
2	2,3-dimethylquinoxaline	425	2.08	*6*
3	phenazine	483	1.23	*7*
4	quinoxaline	545	1.03	*7*
5	dibenzo[*f*,*h*]quinoxaline	591	0.43	

Experimental Section

The preparation and purification of compounds **2** and **3** have been described elsewhere (*4*). Compounds **1**, **4**, and **5** were obtained from Aldrich Chemical Co.; **4** was distilled at 2 mmHg immediately before use, bp 73–76 °C.

Basicities were determined at 25.00 ± 0.02 °C by titration in acetic anhydride with 0.10 N perchloric acid in acetic acid,

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using a Beckman Century SS-1 pH meter (*4*). The end point and the HNP were determined graphically. All runs were carried out in duplicate, with a precision of ±5 mV.

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Preparation of (+)- and (−)-2,3-Dibromo-1-propanols

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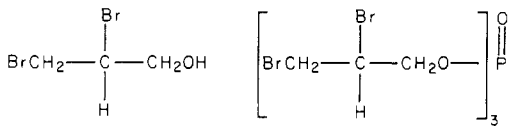
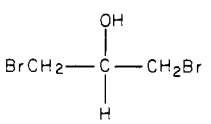
The enantiomers of 2,3-dibromo-1-propanol were obtained by diazotization of the diastereomeric *d*-tartrate salts of 2,3-dibromopropylamine. The products of the reaction contained approximately 13% of the secondary alcohol 1,3-dibromo-2-propanol which was separated by either column chromatography on silica gel or preparative GLC to obtain the primary alcohols (+)-2,3-dibromo-1-propanol ($[\alpha]^{26}_D$ +13.8°) and (−)-2,3-dibromo-1-propanol ($[\alpha]^{24}_D$ −12.8°). NMR and EI mass spectra of the primary and secondary dibromopropanols clearly distinguished the structural isomers from one another. The optical isomers will be used to examine possible stereoselective differences in mutagenic potency, since 2,3-dibromo-1-propanol is a mutagenic metabolite of the potent mutagen and carcinogen tris(2,3-dibromopropyl) phosphate.

2,3-Dibromo-1-propanol (**1**) is a mutagenic metabolite of the



1

2



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potent mutagen, carcinogen, and nephrotoxin tris(2,3-dibromopropyl) phosphate (**2**) (*1*–*4*). Both the alcohol and the ester are oxidized by microsomal cytochrome P-450 to reactive metabolites that apparently bind covalently to tissue macromolecules (DNA, RNA, and protein) (*5*), causing reactions that eventually damage the cell. Because oxidations by cytochrome P-450 are often stereoselective, we were interested in determining the influence of stereochemistry on the toxic properties of 2,3-dibromo-1-propanol and its phosphate ester. Herein we describe the synthesis and purification of the optical isomers of **1**.

Enantiomeric 2,3-dibromo-1-propanols were obtained by the diazotization of the diastereomeric *d*-tartrate salts of 2,3-dibromopropylamine. The products of the diazotization reaction invariably contained about 13% of the secondary alcohol 1,3-dibromo-2-propanol (**3**). Failure to recognize this side-reaction rearrangement by early investigators may account in part for the lower specific rotation values reported for the dextrorotary isomer ranging from 6.5° (*6*) to 7.27° (*7*, *8*) compared to $[\alpha]^{26}_D$ = +13.8° for our purified product. In the 7.27° case there is another possible complicating factor. The bromination of allylamine was carried out on the hydrochloride instead of the hydrobromide salt. A mixture of dibromo and chlorobromo products is formed in this reaction (personal observation).

A similar question is raised regarding the report by Dix and Bresson (*9*) of the synthesis of 2,3-dibromopropylamine hydrochloride by the bromination of allylamine in hydrochloric acid solution. Mass-spectrometric analysis, in our laboratory, of products obtained by the reaction conditions described by Dix and Bresson showed approximately an equimolar mixture of chlorobromo and dibromo products.

Experimental Section

General Methods. Capillary melting points were determined on a Thomas-Hoover apparatus and are uncorrected. NMR spectra were recorded on a Varian EM 360A spectrometer and are expressed in parts per million from Me_4Si as internal standard. Specific rotations were determined with a Jasco DIP-4 digital polarimeter using a 1-dm, 10-mL cell. GLC analyses were performed on a Hewlett-Packard 5840A gas chromatograph using a 6 ft × 2 mm glass column packed with 3% SE-30 on 100–120 mesh Gas Chrom Q at 150 °C oven temperature. Preparative GLC separation was performed on a Varian Aerograph Model 920 using a 20 ft × $^3/_8$ in. stainless-steel column packed with 3% SE-30 on 60–80 mesh Gas Chrom Q, at 130 °C. Mass spectra were recorded on a VG MicroMass 707OH double-focusing instrument. Samples of compounds were introduced by using a direct insertion probe and EI spectra were recorded at a nominal resolution of 1000 (10% valley) using an accelerating voltage of 4 kV, an electron energy of 70 eV, and a trap current of 100 μA. Source temperature was 200 °C.

Materials. *d*-Tartaric acid was "Baker Analyzed" reagent grade. Allylamine was obtained from Aldrich Chemical Co. Silica gel 0.05–0.2 mm was from E. Merck, Germany, and neutral aluminum oxide (Activity I) was from M. Woelm, Germany. Benzene and hexane were distilled prior to use for chromatography.

***2,3-Dibromopropylamine Hydrobromide* (4).** Concentrated HBr (280 mL, 2.4 mol) was added with stirring to a cooled solution of allylamine (2 mol) in 150 mL of H_2O at such a rate that the temperature did not exceed 20 °C. Bromine (320 g, 2 mol) was then added at such a rate that the temperature remained between 15 and 20 °C. A white precipitate developed when less than half of the bromine was added. Bromine addition was continued until yellow color persisted and about 1

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