(10) Andrews, C. E. *Ind. Eng. Chem.* **1918**, *10*, 453.
(11) Werigo, A. *Z. Chem.* **1864**, *7*, 46.
(12) Sumnov, G. *Zh. Fiz. Khim.* **1887**, *19*, 118; *Chem. Centr.* **1887**, 752 (through ref *10*).
(13) Murayama, Y. *J. Pharm. Soc. Jpn.* **1921**, *475*, 769; *Chem. Abstr.* **1922**, *16*, 1568; *Chem. Zentralbl.* **1922**, 199.
(14) Kamm, O. In "Organic Syntheses"; Blatt, A. H., Ed.; Wiley: New York, 1941; Collect. Vol. 1, p 445.
(15) Dewar, M. J. S. In "Molecular Rearrangements"; de Mayo, P., Ed.; Wiley: New York, 1963; Vol. 1, p 309.
(16) Austerweil, G. British Patent 220 953, Oct 15, 1925.
(17) Mann, C. A.; Montonna, R. E.; Larian, M. G. *Trans. Electrochem. Soc.* **1936**, *69*, 367.

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Synthesis of Novel Energetic Compounds. 4

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Reported here are the synthesis and physical properties of eight novel azido compounds. These include four polyalkylene glycol diazides and four tetraazido polyesters. The compounds have been characterized in terms of freezing point, density, refractive index, thermal stability, and impact sensitivity. The properties of these polyazides indicate that these compounds are thermally stable, are relatively insensitive to impact, and possess a wide liquid range.

The synthesis of novel energetic azido compounds has been reported in previous papers of this series (*1-3*). The synthetic chemistry of energetic polyazides has been extended in the current work to include polyalkylene glycol diazides and tetraazido polyesters, and is described herein.

For the synthesis of the polyalkylene glycol diazides from the corresponding glycols, the classical approach of proceeding through the intermediate ditosylate derivative was first considered. From a practical standpoint, the use of the tosylate moiety as a leaving group has the disadvantages of carrying such a large molecular weight material through the reaction sequence, which results in lower yields and higher costs. To circumvent this problem, an alternate, more practical approach for the synthesis of the azido compounds was developed. This approach was based on converting the polyethylene glycol dinitrates, which are readily obtained in quantitative yield from the glycols and nitric acid, to the corresponding diazides:

$$\mathrm{HO(CH_2CH_2O)_\mathit{n}CH_2CH_2OH} \xrightarrow{\mathrm{HNO_3}} \mathrm{O_2NO(CH_2CH_2O)_\mathit{n}CH_2CH_2ONO_2} \xrightarrow{\mathrm{NaN_3}} \mathrm{N_3(CH_2CH_2O)_\mathit{n}CH_2CH_2N_3}$$

On the basis of this work, the series of commercially available polyethylene glycols of molecular weights ranging from 200 to 400 (PEG-200, PEG-300, and PEG-400) have been converted to the corresponding diazides (PEG-200-DA, PEG-300-DA, and PEG-400-DA). Polypropylene glycol 425 diazide (PPG-425-DA) was also prepared and characterized.

The tetraazido polyesters were readily prepared by the esterification of aliphatic and aromatic diacid chlorides with diazidoalkanols. Four examples of this new class of compounds which have been prepared and characterized include bis(2,3-diazidopropyl) adipate (2,3-DAPA), bis(1,3-diazidoisopropyl) adipate (1,3-DAIPA), bis(2,3-diazidopropyl) *o*-phthalate (2,3-DAPP), and bis(1,3-diazidoisopropyl) *o*-phthalate (1,3-DAIPP). The method of preparation is shown in Scheme I.

The identity of these new compounds was confirmed by infrared spectroscopy and elemental analyses. The compounds have been characterized in terms of freezing point, density, refractive index, thermal stability (DSC and weight loss at 74 °C), and impact sensitivity. The properties of these polyazides, as summarized in Tables I and II, indicate that these com-

Scheme I

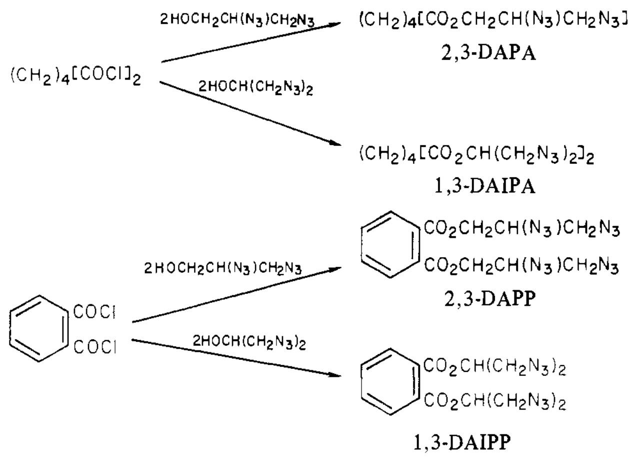

Table I. Properties of Diazide Compounds

	PEG-200-DA	PEG-300-DA	PEG-400-DA	PPG-425-DA
freezing point, °C	<−70	−45	−20	<−80
density, g/cm³	1.12	1.12	1.11	1.03
refractive index at 25 °C	1.4694	1.4685	1.4705	1.4538
DSC (10 °C/min)				
onset of exotherm, °C	175	165	180	160
peak of exotherm, °C	221	218	220	212
weight loss after 24 h at 74 °C, %	6.2	3.1	0	5.8
impact sensitivity,[a] in. lb	>100	>100	>100	ND[b]

[a] By comparison, trimethylolethane trinitrate = 40 in. lb.
[b] ND = not determined.

Table II. Properties of Tetraazido Compounds

	2,3-DAPA	1,3-DAIPA	2,3-DAPP	1,3-DAIPP
freezing point, °C	20	20	−35	−30
density, g/cm³	1.26	1.25	1.31	1.31
refractive index at 25 °C	1.5050	1.5014	1.5516	1.5498
weight loss after 24 h at 74 °C, %	0.5	0.5	ND[b]	ND[b]
impact sensitivity,[a] in. lb	ND[b]	200	95	155

[a] By comparison, trimethylolethane trinitrate = 40 in. lb.
[b] ND = not determined.

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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.

Literature Cited

(1) Witucki, E. F.; Frankel, M. B. *J. Chem. Eng. Data* **1979**, *24*, 247.
(2) Frankel, M. B.; Wilson, E. R. *J. Chem. Eng. Data* **1981**, *26*, 219.
(3) Witucki, E. F.; Frankel, M. B. *J. Chem. Eng. Data* **1982**, *27*, 94.

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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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