crude product was isolated in the usual manner. Chromatography over silica gel with benzene as the eluent gave a fraction which on recrystallization with appropriate solvent (Table I) yielded benzoindolizine derivatives (**9a–h**) in 50–60% yields.

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Registry No. **1a**, 75613-96-6; **1b**, 6276-89-7; **2a**, 57269-96-2; **2b**, 75573-22-7; **2c**, 39954-59-1; **2d**, 7357-47-3; **2e**, 6276-88-6; **5a**, 762-42-5; **5b**, 762-21-0; **7a**, 84801-85-4; **7b**, 84801-86-5; **7c**, 84801-87-6; **7d**, 84801-88-7; **9a**, 84801-89-8; **9b**, 84801-90-1; **9c**, 84801-91-2; **9d**, 84801-92-3; **9e**, 84801-93-4; **9f**, 84801-94-5; **9g**, 84801-95-6; **9h**, 84801-96-7.

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Synthesis of Novel Energetic Compounds. 6

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Reported here are the syntheses and physical properties of five novel energetic aliphatic azido compounds. These include azido nitramines, esters, and amines. The compounds have been characterized in terms of freezing point, refractive index, and impact sensitivity. The properties of these azides indicate that these compounds have a wide liquid range and are relatively insensitive to impact.

The synthesis of novel energetic azido compounds has been reported in previous papers of this series (*1*). This chemistry has been extended in the current work to include azido nitramines, esters, and amines.

The nitramino azides that were prepared included *n*-butyl(2-azidoethyl)nitramine (I), bis[(2-azidoethoxy)methyl]nitramine (II), and 1,12-diazido-3,10-dioxa-5,8-dinitrazadodecane (III). The following are the synthetic routes that were utilized:

$$C_4H_9N(NO_2)CH_2CH_2ONO_2 \xrightarrow{NaN_3} \underset{\text{I}}{C_4H_9N(NO_2)CH_2CH_2N_3}$$

$$N(NO_2)\text{-}[CH_2Cl]_2 + 2HOCH_2CH_2Cl \rightarrow$$

$$N(NO_2)\text{-}[CH_2OCH_2CH_2Cl]_2 \xrightarrow{2NaN_3} \underset{\text{II}}{N(NO_2)\text{-}[CH_2OCH_2CH_2N_3]_2}$$

$$[CH_2N(NO_2)CH_2Cl]_2 + 2HOCH_2CH_2Cl \rightarrow$$

$$[CH_2N(NO_2)CH_2OCH_2CH_2Cl]_2 \xrightarrow{2NaN_3}$$

$$\underset{\text{III}}{[CH_2N(NO_2)CH_2OCH_2CH_2N_3]_2}$$

An azido ester, 6-azidohexyl 6-azidohexanoate (IV), and an azido amine, tris(2-azidoethyl)amine (V), were also synthesized:

$$Br(CH_2)_5COCl + HO(CH_2)_6Cl \rightarrow$$

$$Br(CH_2)_5CO_2(CH_2)_6Cl \xrightarrow{NaN_3} \underset{\text{IV}}{N_3(CH_2)_5CO_2(CH_2)_6N_3}$$

$$N[CH_2CH_2Cl]_3 \xrightarrow{NaN_3} \underset{\text{V}}{N[CH_2CH_2N_3]_3}$$

Table I. Properties of Novel Energetic Azides[a]

compd	$n^{24}{}_D$	fp, °C	impact sensitivity,[b] in.-lb
$C_4H_9N(NO_2)CH_2CH_2N_3$	1.4870	<−78	>150
$N(NO_2)\text{-}[CH_2OCH_2CH_2N_3]_2$	1.5022	<−78	>150
$[CH_2N(NO_2)CH_2OCH_2CH_2N_3]_2$	1.5218	−15	>150
$N_3(CH_2)_5CO_2(CH_2)_6N_3$	1.4723	<−78	>150
$N[CH_2CH_2N_3]_3$	1.5090	−19	60-65

[a] Purity by GC analyses was 99+%. Elemental analyses, in every case, were consistent with the proposed structure. [b] By comparison, trimethylethane trinitrate = 40 in.-lb.

The indentity of these new compounds was confirmed by infrared spectroscopy and elemental analyses. The compounds have been characterized in terms of freezing point, refractive index, and impact sensitivity. The properties of these azides, as summarized in Table I, indicate that these compounds have a wide liquid range and are relatively insensitive to impact.

Experimental Section

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

Isolation and purification were accomplished by liquid chromatography, using silica gel as the adsorbent, 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. Elemental analyses were by Galbraith Laboratories.

n-Butyl(2-azidoethyl)nitramine (I). A mixture of 19.4 g (0.094 mol) of *n*-butyl[2-(nitrooxy)ethyl]nitramine (*2*), 9.4 g (0.145 mol) of sodium azide, and 20 mL of dimethylformamide was heated at 90 °C for 24 h. After the mixture was cooled, the solvent was removed in vacuo. Methylene chloride was added and the insoluble solid was removed by filtration. Re-

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moval of methylene chloride yielded 14.6 g (83% yield) of product.

Bis[(2-chloroethoxy)methyl]nitramine. To 10 g (0.06 mol) of bis(chloromethyl)nitramine (*3*) dissolved in 50 mL of ethylene dichloride at ambient temperature was added dropwise 10.5 g (0.13 mol) of 2-chloroethanol. The reaction mixture was then heated at 85 °C for 120 h. After the mixture was cooled, the solvent was removed, yielding 13 g of yellow oil. This product contained about 60% bis[(2-chloroethoxy)methyl]nitramine. Pure product was obtained via liquid chromatography, using silica gel as the adsorbent, as a pale yellow liquid, $n^{24}{}_D$ 1.4935, in 50% overall yield.

Bis[(2-azidoethoxy)methyl]nitramine (II). A mixture of 2.5 g (0.01 mol) of bis[(2-chloroethoxy)methyl]nitramine, 2.13 g (0.33 mol) of sodium azide, and 25 mL of dimethylformamide was heated at 80 °C for 36 h. After the mixture was cooled, most of the solvent was removed in vacuo. Methylene chloride was added and the insoluble solid was removed via centrifugation. The methylene chloride solution was then washed 4 times with water to remove the remaining dimethylformamide. Removal of methylene chloride yielded 2.5 g (95% yield) of product.

1,12-Dichloro-3,10-dioxa-5,8-dinitrazadodecane. A mixture of 10 g (0.04 mol) of 1,6-dichloro-2,5-dinitrazahexane (*3*), 6.8 g (0.085 mol) of 2-chloroethanol, and 50 mL of 1,2-dichloroethane was heated at 80 °C for 72 h. After the mixture was cooled, the solvent was removed, yielding 12.2 g (90% yield) of product, $n^{27}{}_D$ 1.5147.

1,12-Diazido-3,10-dioxa-5,8-dinitrazadodecane (III). A mixture of 2 g (0.006 mol) of 1,12-dichloro-3,10-dioxa-5,8-dinitrazadodecane, 1.16 g (0.018 mol) of sodium azide, and 25 mL of dimethylformamide was heated at 85 °C for 24 h. After the mixture was cooled, the insoluble solid was removed by filtration. Methylene chloride was added and the solvent was removed by washing with water. Removal of methylene chloride yielded 1.8 g (87%) of product.

6-Chlorohexyl 6-Bromohexanoate. To 10 g (0.047 mol) of 6-bromocaproyl chloride dissolved in 50 mL of ethylene dichloride at ambient temperature was added dropwise 6.4 g (0.047 mol) of 6-chlorohexanol-1. The resulting reaction mixture was heated at reflux for 20 h. Solvent was removed, yielding 16.8 g of crude 6-chlorohexyl 6-bromohexanoate. Purification of this crude material was accomplished by an initial distillation which removed byproduct, 1,6-dichlorohexane, followed by liquid chromatography involving silica gel as the adsorbent. Pure product was obtained as a near colorless liquid in 70% yield, $n^{23}{}_D$ 1.4780.

6-Azidohexyl 6-Azidohexanoate (IV). A mixture of 10.8 g (0.034 mol) of 6-chlorohexyl 6-bromohexanoate, 6.7 g (0.103 mol) of sodium azide, and 100 mL of dimethylformamide was heated at 80 °C for 16 h. After the mixture was cooled, the solvent was removed in vacuo. Methylene chloride was added and the insoluble solid was removed via centrifugation. The solvent was then removed, yielding 9.6 g (99% yield) of product.

Tris(2-azidoethyl)amine (V). A mixture of 35.2 g (0.17 mol) of tris(2-chloroethyl)amine (*4*), 37.0 g (0.57 mol) of sodium azide, and 100 mL of dimethylformamide was heated at 95 °C for 2 h. The reaction mixture was cooled, diluted with 100 mL of methylene chloride, and washed 6 times with water to remove the inorganic salts and the dimethylformamide. The methylene chloride solution was dried over anhydrous sodium sulfate and passed through a column of neutral alumina to yield a colorless solution. Concentration of the solution gave 31.8 g (83%) of pale yellow oil.

Registry No. **2**, 82486-82-6; **4**, 555-77-1; I, 84928-98-3; II, 84487-87-6; III, 84487-88-7; IV, 84487-84-3; V, 84928-99-4; bis(chloromethyl)nitramine, 13126-15-3; sodium azide, 26628-22-8; 2-chloroethanol, 107-07-3; bis[(2-chloroethoxy)methyl]nitramine, 84487-86-5; 1,6-dichloro-2,5-dinitrazahexane, 13237-32-6; 1,12-dichloro-3,10-dioxa-5,8-dinitrazadodecane, 84487-89-8; 6-chlorohexyl 6-bromohexanoate, 84487-83-2; 6-bromocaproyl chloride, 22809-37-6; 6-chloro-1-hexanol, 2009-83-8.

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Correction

Isobaric Vapor–Liquid Equilibria of the *p*-Xylene–1,1,2,2-Tetrachloroethane System. M. V. Rao and D. S. Viswanath,* *J. Chem. Eng. Data* **1982**, *27*, 417–9.

An error has occurred in reporting the constants for eq 2. The constant a_1 should be 128.9957 and a_2 should be −693.1446.