carbonate solution. Sodium borohydride (0.8 mmol) was then added and the slurry vigorously stirred at room temperature until disappearance of the starting material (TLC). Water (10 mL) was then added and the mixture thoroughly extracted with ethyl ether. The ethereal layer was then washed with water (3 × 10 mL) and dried over Na_2SO_4. After evaporation of the solvent, the purity of the resulting alcohols was determined by ^1H NMR or VPC analysis. Rotations were taken at 25 °C, and enantiomeric excesses were determined from the integral ratios of selected ^1H NMR (200 MHz) signals of diastereomeric α-methoxy-α-(trifluoromethyl)phenylacetic acid esters[9] (entries 6, 8, and 11 of Table I) or of the alcohol in the presence of tris[3-((trifluoromethyl)hydroxymethylene-*d*)camphorato]europium(III) (entry 13).

Acknowledgment. We thank E. Castiglione for his skilled technical assistance and the Ministry of Public Education, Italy, for financial support.

Registry No. $PhCOCH_3$–(β-CD) 1:1 complex, 97150-81-7; $PhCOCH_2CH_3$–(β-CD) 1:1 complex, 97150-82-8; $PhCOCH_2CH_2CH_3$–(β-CD) 1:1 complex, 97150-83-9; $PhCH_2COCH_3$–(β-CD) 1:1 complex, 97150-84-0; $PhCH_2CH_2COCH_3$–(β-CD) 1:1 complex, 97150-85-1; (*E*)-$PhCH{=}CHCOCH_3$–(β-CD) 1:1 complex, 97150-86-2; (*E*)-$PhCH{=}CHCOCH_3$–[heptakis(2,6-di-*O*-methyl)-β-cyclodextrin] 1:1 complex, 97150-87-3; *m*-$CH_3C_6H_4COCH_3$–(β-CD) 1:1 complex, 97150-88-4; 1-$(C_{10}H_7)COCH_3$–(β-CD) 1:1 complex, 97150-89-5; 2-$(C_{10}H_7)COCH_3$–(β-CD) 1:1 complex, 97150-90-8; 1-$(C_{10}H_7)$-$CH{=}CHCOCH_3$–(β-CD) 1:1 complex, 97150-91-9; $FcCOCH_3$-(β–CD) 1:1 complex, 92512-21-5; $FcCH{=}CHCOCH_3$–(β-CD) 1:1 complex, 97150-92-0; *n*-$C_6H_{13}COCH_3$–(β-CD) 1:1 complex, 97150-93-1; (*S*)-$PhCH(OH)CH_3$, 1445-91-6; (*R*)-$PhCH(OH)CH_2CH_3$, 1565-74-8; (*R*)-$PhCH(OH)CH_2CH_2CH_3$, 22144-60-1; (*S*)-$PhCH_2CH(OH)CH_3$, 1517-68-6; (*S*)-$PhCH_2CH_2CH(OH)CH_3$, 22148-86-3; (*S*)-(*E*)-$PhCH{=}CHCH(OH)CH_3$, 81176-43-4; (*R*)-(*E*)-$PhCH{=}CHCH(OH)CH_3$, 62413-47-2; (*R*)-1-$(C_{10}H_7)CH(OH)CH_3$, 42177-25-3; (*S*)-2-$(C_{10}H_7)CH(OH)CH_3$, 27544-18-9; (*S*)-$FcH(OH)CH_3$, 33136-66-2; (*S*)-*n*-$C_6H_{13}CH(OH)CH_3$, 6169-06-8; $NaBH_4$, 16940-66-2.

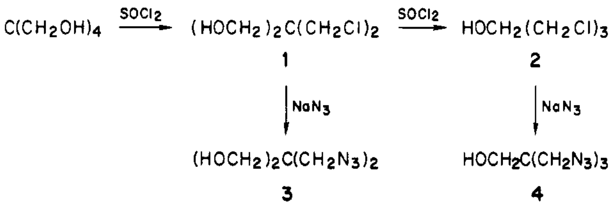
Synthesis of Novel Energetic Compounds. 7. Azido Derivatives of Pentaerythritol

Edgar R. Wilson and Milton B. Frankel*

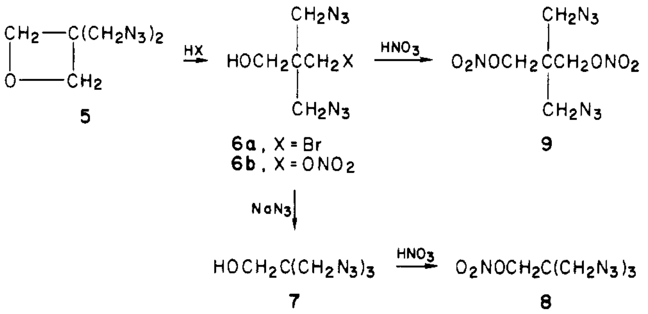
Rocketdyne, A Division of Rockwell International,
Canoga Park, California 91304

Received January 25, 1985

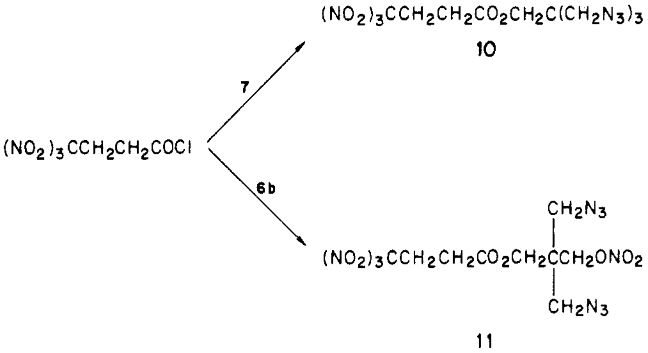
The synthesis of novel energetic azido compounds has been reported in previous papers of this series.[1] In the current work, it was of interest to prepare diazido and triazido derivatives of pentaerythritol. The initial approach for the synthesis of these compounds was based on the conversion of pentaerythritol to the dichloro (1) and trichloro (2) derivatives,[2] followed by subsequent reaction with sodium azide to give pentaerythritol diazide (3) and pentaerythritol triazide (4). However, this method for the preparation of 1 and 2 gave mixtures of mono-, di-, tri-, and tetrasubstituted products, which were difficult to separate and purify. Consequently, the synthesis of the corresponding azido compounds 3 and 4 by this process did not appear promising, and a better method of synthesis was sought.



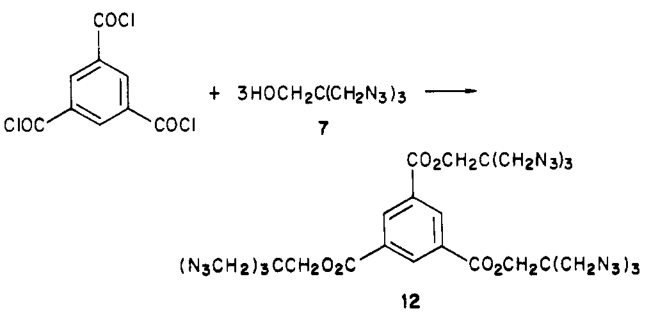
In previous work in this laboratory, a facile synthesis of bis(3,3-azidomethyl)oxetane (5) was reported.[3] It has now been found that diazido derivatives of pentaerythritol can be prepared cleanly and in high yield by the treatment of 5 with inorganic acids. In this manner, pentaerythritol diazide monobromide (**6a**) and pentaerythritol diazide mononitrate (**6b**) were prepared. Treatment of **6a** with sodium azide gave pentaerythritol triazide (**7**), which was subsequently nitrated to pentaerythritol triazide mononitrate (**8**). Nitration of **6b** yielded pentaerythritol diazide dinitrate (**9**).



The general utility of the alcohols **7** and **6b** as precursors for the preparation of energetic esters was demonstrated. Both alcohols reacted readily with 4,4,4-trinitrobutyryl chloride to form the polyazido/polynitro-substituted esters tris(2,2,2-azidomethyl)ethyl and 3-(nitrooxy)-2,2-bis(azidomethyl)propyl 4,4,4-trinitrobutyrates (**10** and **11**, respectively) in high yields.



Further demonstration of the reactivity of **7** was obtained from its reaction with 1,3,5-benzenetricarboxylic acid chloride to give 1,3,5-tris(2,2,2-azidomethyl)ethyl benzenetricarboxylate (**12**).



Experimental Section

General Procedures. Caution! Most of the products and starting materials described are explosives of moderate to con-

---

[1] Previous paper in this series: Witucki, E. F.; Wilson, E. R.; Flanagan, J. E.; Frankel, M. B. *J. Chem. Eng. Data* **1983**, *28*, 285.

[2] Mooradian, A.; Cloke, J. B. *J. Am. Chem. Soc.* **1945**, *67*, 942.

[3] Frankel, M. B.; Wilson, E. R. *J. Chem. Eng. Data* **1981**, *26*, 219.

0022-3263/85/1950-3211$01.50/0

siderable sensitivity to initiation by impact, shock, friction, and other means and should be handled with care. All reactions should be carried out behind safety shields. Isolation and purification were accomplished in most cases 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 HP 5840A instrument using a 6 ft × 6 mm glass column packed with 3% OV 210 on Chromosorb T. Microanalyses were carried out by Galbraith Laboratories, Knoxville, TN.

3,3-Bis(azidomethyl)oxetane (5). A mixture of 59.5 g (0.38 mol) of distilled 3,3-bis(chloromethyl)oxetane (Columbia Chemical Co.), 54.3 g (0.84 mol) of sodium azide, and 200 mL of dimethylformamide was heated at 90–100 °C for 2 h. The reaction mixture was cooled to ambient temperature, poured into 1 L of water, and extracted with 200 mL of methylene chloride. The methylene chloride extract was washed twice with 500-mL portions of water, dried over anhydrous sodium sulfate, and concentrated. The resultant pale yellow oil was distilled to give 48.3 g (76%) of colorless liquid: bp 79–81 °C (0.4 mmHg); $n^{25}{}_{\mathrm{D}}$ 1.5054.

Anal. Calcd for $C_5H_8N_6O$: C, 35.71; H, 4.80; N, 49.98. Found: C, 35.28; H, 4.64; N, 49.67.

Pentaerythritol Diazide Monobromide (6a). To a mixture of 258 g (1.5 mol) of 47% hydrobromic acid and 150 mL of methylene chloride was added dropwise 168 g (1.0 mol) of bis(3,3-azidomethyl)oxetane (5) in 30 min. The reaction temperature rose from 24 to 38 °C. After the addition was complete, the reaction mixture was refluxed for 2 h. The organic layer was separated, washed with water and dilute sodium bicarbonate solution, dried over anhydrous sodium sulfate, and concentrated to give 240.0 g (96.5%) of yellow oil, $n^{24}{}_{\mathrm{D}}$ 1.5436. The infrared spectrum was consistent for the expected structure with strong absorptions at 3.0 (hydroxyl) and 4.8 μm (azido).

Anal. Calcd for $C_5H_9BrN_6O$: C, 24.11; H, 3.64; Br, 32.08. Found: C, 24.27; H, 4.15; Br, 31.81.

Pentaerythritol Triazide (7). A mixture of 189.4 g (0.76 mol) of pentaerythritol diazide monobromide (**6a**), 98.9 g (1.52 mol) of sodium azide, and 570 mL of dimethyl sulfoxide was heated, with good stirring, at 85–90 °C for 48 h. The reaction mixture was cooled to ambient temperature and diluted with 500 mL of water and 300 mL of methylene chloride. The organic phase was separated and washed with ten 1-L portions of water to remove the inorganic salts and the dimethyl sulfoxide. The methylene chloride solution was dried over anhydrous sodium sulfate, passed through a column packed with Davidson Grade 62 silica gel, prewetted with methylene dichloride, and concentrated to give 129.6 g (77%) of colorless oil, $n^{2}{}_{\mathrm{D}}$ 1.5319. The infrared spectrum was consistent for the expected structure with strong absorptions at 3.0 (hydroxyl) and 4.8 μm (azido).

Anal. Calcd for $C_5H_9N_9O$: C, 28.43; H, 4.30, N, 59.69. Found: C, 28.03; H, 4.22; N, 60.03.

Pentaerythritol Triazide Mononitrate (8). To a solution of 0.8 g (7.8 mmol) of acetic anhydride in 4 mL of methylene chloride was added 0.34 g (5.2 mmol) of 98% nitric acid at 0–5 °C. A solution of 1.0 g (4.7 mmol) of pentaerythritol triazide (7) in 5 mL of methylene chloride was added dropwise in 10 min, keeping the temperature at 0–5 °C. After addition was complete, the reaction mixture was allowed to warm to ambient temperature, stirred for an additional 30 min, and diluted with 10 mL of ice–water. The organic layer was separated and washed with dilute sodium bicarbonate solution and water. The methylene chloride solution was dried over anhydrous sodium sulfate, passed through a column of 150 mesh and Brockmann 1 neutral alumina column, and concentrated to give 1.07 g (89.2%) of colorless oil, $n^{22.5}{}_{\mathrm{D}}$ 1.5245. The infrared spectrum was consistent for the expected structure with strong absorptions at 4.8 (azido) and 6.15 μm (nitrate).

Anal. Calcd for $C_5H_8N_{10}O_3$: C, 23.44; H, 3.15; N, 54.68. Found: C, 23.65; H, 3.15; N, 54.69.

Pentaerythritol Diazide Mononitrate (6b). To a solution of 16.8 g (0.1 mol) of bis(3,3-azidomethyl)oxetane (5) in 20 mL of methylene chloride was added 18.0 g (0.2 mol) of 70% nitric acid dropwise in 30 min. The temperature rose from 22 to 30 °C during the addition. The reaction mixture was stirred at ambient temperature for 69 h, at which time GC analysis showed that all of the starting material had disappeared. The reaction mixture was washed with 50 mL water, 50 mL of dilute sodium bicarbonate, and 50 mL of water, dried over magnesium sulfate, and concentrated to give 17.9 g (77.5%) of yellow oil, $n^{25}{}_{\mathrm{D}}$ 1.5186. The infrared spectrum was consistent for the expected structure with strong absorptions at 3.0 (hydroxyl), 4.8 (azido), and 6.15 μm (nitrate).

Anal. Calcd for $C_5H_9N_7O_4$: C, 25.98; H, 3.92; N, 42.41. Found: C, 26.13; H, 3.90; N, 42.49.

Pentaerythritol Diazide Dinitrate (9). To a solution of 0.73 g (0.0072 mol) of acetic anhydride in 4 mL of methylene chloride was added 0.31 g (0.21 mol) of 98% nitric acid at 0–5 °C. A solution of 1.0 g (0.0043 mol) of pentaerythritol diazide mononitrate (**6b**) in 2 mL of methylene chloride was added dropwise in 10 min, keeping the temperature at 0–5 °C. The reaction mixture was stirred for an additional 5 min at 0–5 °C and then allowed to warm to ambient temperature. The reaction mixture was diluted with 10 mL of ice–water; the organic phase was separated and washed with dilute sodium bicarbonate solution and water. The methylene chloride solution was dried over magnesium sulfate, passed through a column of 150 mesh and Brockmann 1 neutral alumina, and concentrated to yield 1.0 g (84%) of almost colorless oil, $n^{22.5}{}_{\mathrm{D}}$ 1.5161. The infrared spectrum was consistent for the expected structure with strong absorptions at 4.8 (azido) and 6.15 μm (nitrate).

Anal. Calcd for $C_5H_8N_8O_6$: C, 21.74; H, 2.92; N, 40.58. Found: C, 22.40; H, 3.17; N, 40.79.

Tris[2,2,2-(Azidomethyl)ethyl] 4,4,4,-Trinitrobutyrate (10). A solution of 3.81 g (16 mmol) of 4,4,4-trinitrobutyryl chloride,[4] 3.06 g (14 mmol) of pentaerythritol triazide (7), and 10 mL of ethylene dichloride was refluxed for 70 h. At this time, GC analysis showed no starting materials. The reaction mixture was diluted with 20 mL of methylene chloride and stirred with 20 mL of dilute sodium bicarbonate solution, for 1 h at ambient temperature. The organic phase was separated, washed with water, dried over magnesium sulfate, passed through a column of 150 mesh and Brockmann neutral alumina, and concentrated to give a 5.35 g (91.9%) of yellow oil, $n^{21}{}_{\mathrm{D}}$ 1.5194. The infrared spectrum was consistent for the expected structure with strong absorption at 4.8 (N_3), 5.8 (C=O), and 6.35 μm (NO_2).

Anal. Calcd for $C_9H_{12}N_{12}O_8$: C, 25.97; H, 2.91; N, 40.38. Found: C, 25.73; H, 2.78; N, 40.52.

3-(Nitrooxy)-2,2-bis(azidomethyl)propyl 4,4,4-Trinitrobutyrate (11). A solution of 22.3 g (92 mmol) of 4,4,4-trinitrobutyryl chloride, 19.4 g (84 mmol) of pentaerythritol diazide mononitrate, and 65 mL of ethylene dichloride was refluxed for 90 h. The cooled reaction mixture was washed with water, dilute sodium bicarbonate solution, and water, dried over magnesium sulfate, and concentrated to yield 34.6 g (94.5%) light yellow oil, $n^{26}{}_{\mathrm{D}}$ 1.5108. The infrared spectrum was consistent with the expected structure.

Anal. Calcd for $C_9H_{12}N_{10}O_{11}$: C, 24.78; H, 2.77; N, 32.11. Found: C, 25.31; H, 2.84; N, 32.79.

Tris[2,2,2-(azidomethyl)ethyl] 1,3,5-Benzenetricarboxylate (12). To a solution of 5.31 g (20 mmol) of 1,3,5-benzenetricarboxylic acid chloride, 13.07 g (62 mmol) of pentaerythritol triazide, and 30 mL of ethylene dichloride was added dropwise 4.9 g (62 mmol) of pyridine. The reaction temperature was maintained at 15–25 °C by external cooling with an ice bath. After the addition was complete, the reaction mixture was stirred overnight at ambient temperature, then washed with water, dilute sodium bicarbonate, and water, dried over anhydrous sodium sulfate, and passed through a column packed with Davidson Grade 62 silica gel prewetted with ethylene dichloride. Concentration of the solution gave 12.3 g (77.9%) of crude oil. Purification from a chloroform–methanol solution gave crystals, mp 65–68 °C.

Anal. Calcd for $C_{21}H_{27}N_{27}O_3$: C, 36.50; H, 3.42; N, 47.91. Found: C, 36.54; H, 3.49; N, 47.74.

Registry No. 5, 17607-20-4; **6a**, 96915-34-3; **6b**, 96915-35-4; 7, 96915-36-5; 8, 96915-37-6; **9**, 96915-38-7; **10**, 96915-39-8; 11, 96915-40-1; **12**, 96915-41-2; 3,3-bis(chloromethyl)oxetane, 78-71-7; 4,4,4-trinitrobutyryl chloride, 36638-86-5; 1,3,5-benzenetricarboxylic acid chloride, 4422-95-1.

---

[4] Gold, M. H.; Frankel, M. B.; Linden, G. B.; Klager, K. *J. Org. Chem.* **1962**, *27*, 334.