2 H), 3.99 (t, 2 H); IR (NaCl) 1740 cm^{-1} (C=O).

β-Methyl-δ-valerolactone (7a): ^{13}C NMR ($CDCl_3/Me_4Si$) δ 172.3 (s), 62.1 (t), 41.3 (d), 35.0 (t), 27.4 (t), 19.5 (q); ^1H NMR ($CDCl_3/Me_4Si$) δ 0.97 (d, 3 H), 1.33–2.40 (m, 5 H), 4.18 (t, 2 H); IR (NaCl) 1739 cm^{-1} (C=O).

1,2-Phthalide (10): ^{13}C NMR ($CDCl_3/Me_4Si$) δ 170.9 (s), 146.4 (s), 133.8 (d), 128.7 (d), 125.3 (s), 125.2 (d), 122.1 (d), 69.6 (t); ^1H NMR ($CDCl_3/Me_4Si$) δ 5.38 (s, 2 H), 7.40–8.10 (m, 4 H); IR (NaCl) 1760 cm^{-1} (C=O).

1,8-Naphthalide (12): ^{13}C NMR ($CDCl_3/Me_4Si$) δ 163.0 (s), 134.1 (s), 132.3 (s), 132.0 (s), 127.9 (s), 126.2 (d), 125.9 (d), 125.5 (d), 125.3 (d), 125.3 (d), 120.3 (d), 68.9 (t); ^1H NMR ($CDCl_3/Me_4Si$) δ 5.71 (s, 2 H), 7.17–8.50 (m, 6 H); IR (NaCl) 1725 cm^{-1} (C=O).

β-Methyl-γ-butyrolactone (5a): ^{13}C NMR ($CDCl_3/Me_4Si$) δ 179.1 (s), 73.6 (t), 35.0 (t), 29.3 (d), 14.1 (g); ^1H NMR ($CDCl_3/Me_4Si$) δ 1.10 (d, 3 H), 2.00–2.90 (m, 3 H), 3.82–4.03 (d, 2 H); IR (NaCl) 1775 cm^{-1} (C=O).

α-Methyl-γ-butyrolactone (4a): ^{13}C NMR ($CDCl_3/Me_4Si$) δ 176.3 (s), 65.1 (t), 33.1 (d), 29.0 (t), 16.8 (q); ^1H NMR ($CDCl_3/Me_4Si$) δ 1.29 (d, 3 H), 1.82–2.90 (m, 3 H), 4.03–4.43 (m, 2 H); IR (NaCl) 1740 cm^{-1} (C=O).

β-Phenyl-γ-butyrolactone (5b): ^{13}C NMR ($CDCl_3/Me_4Si$) δ 175.3 (s), 135.5 (s), 127.3 (d), 126.6 (d), 125.4 (d), 65.4 (t), 44.3 (d), 30.3 (t); ^1H NMR ($CDCl_3/Me_4Si$) δ 2.60–2.98 (d, 2 H), 3.70–4.71 (m, 3 H), 7.15–7.42 (m, 5 H); IR (NaCl) 1770 cm^{-1} (C=O).

α-Phenyl-γ-butyrolactone (4b): ^{13}C NMR ($CDCl_3/Me_4Si$) δ 176.3 (s), 138.3 (s), 127.8 (d), 127.6 (d), 12693 (d), 72.8 (t), 39.8 (d), 34.5 (t); ^1H NMR ($CDCl_3/Me_4Si$) δ 2.30–2.79 (m, 2 H), 3.52–4.53 (m, 3 H), 7.20–7.40 (m, 5 H); IR (NaCl) 1760 cm^{-1} (C=O).

α,α-Dimethyl-δ-valerolactone (7b): ^{13}C NMR ($CDCl_3/Me_4Si$) δ 176.6 (s), 64.7 (t), 34.0 (s), 26.3 (t), 19.6 (t), 14.1 (q); ^1H NMR ($CDCl_3/Me_4Si$) δ 1.23 (s, 6 H), 1.79–2.10 (m, 4 H), 4.45 (t, 2 H); IR (NaCl) 1730 cm^{-1} (C=O).

γ,γ-Dimethyl-δ-valerolactone (8): ^{13}C NMR ($CDCl_3/Me_4Si$) δ 170.0 (s), 59.3 (t), 26.7 (s), 23.8 (t), 19.9 (t), 13.1 (q); ^1H NMR ($CDCl_3/Me_4Si$) δ 0.91 (s, 6 H), 1.62 (t, 2 H), 3.72 (s, 2 H); IR (NaCl) 1730 cm^{-1} (C=O).

Registry No. **1a**, 110-63-4; **1b**, 111-29-5; **1c**, 629-11-8; **1d**, 112-47-0; **1e**, 5675-51-4; **2a**, 542-28-9; **2b**, 502-44-3; **2c**, 539-87-7; **2d**, 1725-03-7; **2e**, 1725-04-8; **3a**, 2938-98-9; **3b**, 6837-05-4; **4a**, 1679-47-6; **4b**, 6836-98-2; **5a**, 1679-49-8; **5b**, 1008-73-7; **6a**, 4457-71-0; **6b**, 3121-82-2; **7a**, 1121-84-2; **7b**, 4830-05-1; **8**, 1679-55-6; **9**, 612-14-6; **10**, 87-41-2; **11**, 2026-08-6; **12**, 518-86-5; **13**, 6117-80-2; **14**, 116503-38-9; **15**, 626-95-9; **16**, 1071-73-4; **17**, 108-29-2; **19**, 18545-25-0; CWP, 115031-77-1; WPA, 1343-93-7; CPC, 123-03-5; CMP, 88418-08-0.

A Convenient Synthesis of "Bis-homotris": 4-Amino-4-[1-(3-hydroxypropyl)]-1,7-heptanediol and 1-Azoniapropellane[1]

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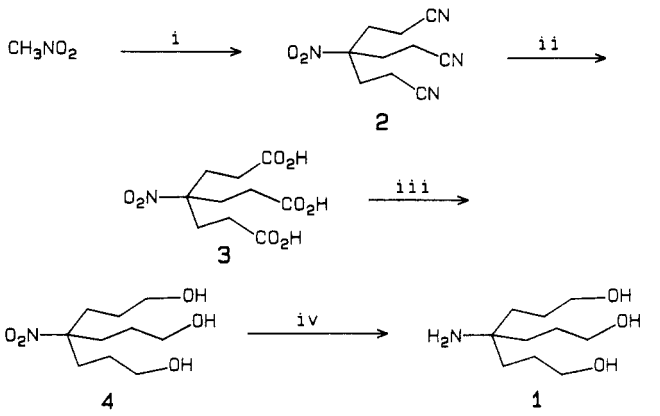
One of our research goals is the synthesis of unimolecular micelles based on the cascade methodology,[2] which involves successive multiplicative synthetic sequences,[3-5] in which an alkyl halide, or its equivalent, is alkylated with the carbanion of a trialkyl methanetricarboxylate, and then amidated with an appropriate multifunctional amine, such as tris(hydroxymethyl)aminomethane ("tris"). Subsequent transformation of the hydroxyl groups to better nucleofuges would allow repetition of the process; however, the nucleophilic displacement of such leaving groups (i.e. bromide) by a *C*-nucleophile does not readily occur under "reasonable" reaction conditions (<100 °C) due to the neopentyl moiety.[6] Tomalia, Hall, and co-workers[7] circumvented this limitation by the use of a "tied-back" oxy anion nucleophile under rigorous conditions.

It was initially surmised that a single carbon homologation[8] of "tris" should circumvent the substitution problem associated with a bulky carbon nucleophile. Unfortunately, work toward this end, confirmed by a search of the literature,[9] indicated that complete substitution by large nucleophiles, e.g. iodide, was still precluded due to steric hindrance. To bypass this problem, a convenient four-step, high-yield (93% overall) route to the convenient cascade building block, 4-amino-4-[1-(3-hydroxypropyl)]-1,7-heptanediol ("bis-homotris") (**1**) was devised and is reported herein.

Tris(β-cyanoethyl)nitromethane (**2**) was prepared (51%) by using a modified procedure adopted from Bruson and Riener,[10] in which the anion of nitromethane underwent a Michael reaction with 3 equiv of acrylonitrile, with tetrabutylammonium hydroxide.[11] Rigorous purification of **2** is imperative to obviate the arduous task of purifying subsequent products. Acid hydrolysis of **2** smoothly afforded (94%) the nitro triacid **3**, which was identified by the appearance in the ^{13}C NMR spectrum of a peak at 173.7 ppm attributable to the carbonyl carbon. Mild borane–THF[12] reduction of **3** gave triol **4** as evidenced by the ^{13}C NMR absorption at 60.6 ppm (Scheme I).

Various reduction procedures are available for the conversion of nitroalkanols to aminoalkanols,[13-22] employing

Scheme I[a]



[a] (i) $Bu_4N^+HSO_4^-$, KOH, H_2O, dioxane, 80–85 °C; (ii) HCl (concentrated), reflux; (iii) BH_3, THF, N_2, 0–25 °C; (iv) T-1 Raney Ni, EtOH, 25 °C, 72 h.

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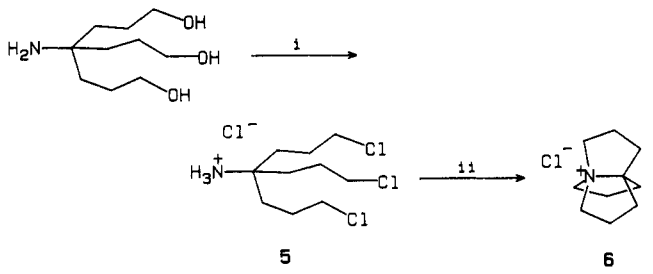
Scheme II[a]



5 6

[a] (i) $SOCl_2$, 10 min, 25 °C; (ii) MeCN, K_2CO_3, 18 h, reflux.

platinum, palladium, or Raney nickel catalysts. None of these methods was satisfactory due to either high pressures, incomplete reduction, or undesirable side products. The requirements of a clean and quantitative reduction were realized, however, when specially generated[23] T-1 Raney nickel was used. With this activated catalyst **4** was reduced (97%) to bis-homotris (**1**), which was confirmed by an upfield shift of the quaternary carbon in the ^{13}C NMR spectrum (**4**, δ 94.7; **1**, δ 52.4).

The amino triol **1** was perceived as a convenient precursor for the preparation of 1-azoniatricyclo[3.3.3.0]undecane, a compound known to possess phase transfer properties.[24] Previous syntheses focused on the separate construction of each ring[25,26] with silver oxide employed as a base to effect quaternization. Our method involves functionalization of bis-homotris to obtain suitable leaving groups and subsequent quaternization of the amine via three intramolecular nucleophilic substitutions (see Scheme II).

Reaction of **1** with excess thionyl chloride yielded 94% of the crude tris(chloride) ammonium salt **5** as a hygroscopic oil, which was substantiated by shifts in the ^{13}C NMR absorptions of the α- and δ-carbons to 58.5 and 44.2 ppm, respectively. Without further purification, **5** was directly converted (82% from **1**) to the 1-azoniapropellane, **6**.

Characterization of the synthetic intermediates was readily accomplished by ^{13}C NMR spectroscopy. Assignments of the β- and γ-carbon atoms (see Scheme II) were based on calculated values,[27] thus the β-carbons of **1**–**6** were assigned further downfield relative to the γ-carbon signals. For example, the β- and γ-carbons of the amino triol **1** were assigned to the 36.3 ppm (calcd 37.6 ppm) and 26.8 ppm (calcd 28.2 ppm) resonances, respectively. The downfield chemical shift for the β-carbon is probably due to its proximity to the center of branching.[28]

Experimental Section

General Comments. Melting point data were obtained from samples in capillary tubes with a Gallenkamp melting pointing apparatus (MFB-595) and are uncorrected. ^1H and ^{13}C NMR data were recorded on an IBM NR-80 spectrometer and were obtained in Me_2SO-d_6 solutions with Me_4Si, as the internal standard, unless otherwise indicated. Mass spectral (MS) data were obtained at 70 eV by Burt Wolf (FSU) on a Finnigan 4510 GC-mass spectrometer (assignment, relative intensity). IR data were obtained on an IBM IR30 spectrometer.

Tris(β-cyanoethyl)nitromethane (2) was prepared by the procedure of Bruson and Riener[10] except that a solution of KOH (4.5 g) in H_2O (10 mL) was added, in one portion, to a stirred solution of nitromethane (20 g), dioxane (100 mL), acrylonitrile (100 mL), tetrabutylammonium hydrogen sulfate (12 g), and H_2O (10–20 mL). (***Caution***: *This reaction is very exothermic and should only be performed in a well ventilated hood. Application of the ice–water bath should commence at or near 50–60 °C*): mp 116.0–118.0 °C ($CH_3CN/CHCl_3$) (lit.[26] mp 114 °C); 84%; ^1H NMR δ 2.30 (m, $CH_2C{\equiv}N$, 6 H), 2.60 (m, $CH_2CH_2C{\equiv}N$, 6 H); IR 2249, 1607, 1487 cm^{-1}; ^{13}C NMR δ 119.3 ($C{\equiv}N$), 91.0 (CNO_2), 29.3 ($CH_2CH_2C{\equiv}N$), 11.5 ($CH_2C{\equiv}N$); MS, *m/e* 174 ($M^+ - NO_2$, 94).

4-[1-(2-Carboxyethyl)]-4-nitroheptanedioic Acid (3). A mixture of nitrile **2** (15.0 g) and concentrated HCl (65 mL) was refluxed 45 min and then cooled to 5 °C. The white solid was filtered, and washed with (4 × 150 mL) cold H_2O and dried in vacuo for 18–24 h to give (94%) the pure acid: 17.7 g; mp 183.0–185.5 °C (lit.[26] mp 186 °C); ^1H NMR δ 2.18 (s, CH_2CH_2C-O_2H, 12 H), 11.58 (br s, CO_2H, 3 H); IR (Nujol mull) 3450–2500, 1701, 1532, 1458, 947 cm^{-1}; ^{13}C NMR δ 173.7 ($C{=}O$), 93.2 (CNO_2), 30.1 ($CH_2CH_2CO_2H$), 28.5 (CH_2CO_2H); MS, *m/e* 260 ($M^+ - OH$, 1).

4-Nitro-4-[1-(3-hydroxypropyl)]-1,7-heptanediol (4). A stirred THF (50 mL, dried over Na; 24 h) solution of triacid **3** (1.0 g, 3.6 mmol) was cooled to 0 °C with an ice–salt bath, and a BH_3–THF solution (1.0 M; 11.9 mL, 11.9 mmol) was added dropwise. After formation of a white precipitate, the temperature was allowed to rise to 25 °C. Stirring was continued another 30 min at which time H_2O was slowly added until the solid had disappeared. Saturated $NaHCO_3$ (25 mL) was then added, and the solvent was removed in vacuo. The viscous slurry was dried in vacuo; the resultant solid was triturated with hot absolute EtOH (3 × 60 mL) and filtered. The combined organic extract was concentrated to give (95%) the pure nitro triol: 800 mg; bp >150 °C (0.3 mm) dec; ^1H NMR δ 1.30 (m, CH_2CH_2OH, 6 H), 1.92 (m, $CH_2CH_2CH_2OH$, 6 H), 3.39 (t, CH_2OH, J = 6.0 Hz, 6 H), 4.12 (br s, OH, 3 H); IR (neat) 3600–3050, 1533, 1454, 1061 cm^{-1}; ^{13}C NMR δ 94.7 (CNO_2), 60.6 (CH_2OH), 31.2 ($CH_2CH_2CH_2OH$), 26.8 (CH_2CH_2OH); MS, *m/e* 189 ($M^+ - NO_2$, 6). Anal. Calcd for $C_{10}H_{21}NO_5$: C, 51.06; H, 8.94; N, 5.96. Found: C, 50.89; H, 8.85; N, 5.99.

4-Amino-4-[1-(3-hydroxypropyl)]-1,7-heptanediol (1). A solution of nitro triol **4** (4.7 g, 20 mmol), absolute EtOH (150 mL), and T-1 Raney Ni[23] (2–3 g) was reduced under a H_2 atmosphere in a Parr hydrogenator at 3 atm for 72 h at 25 °C or until hydrogen uptake subsided. The catalyst was cautiously filtered through a Celite pad (pyrophoric when dry). The solvent was removed in vacuo, and the resultant viscous liquid was dried in vacuo to yield (98%) of the crude aminotriol (4.1 g), which was distilled (Kugelrohr) to afford (82%) bis-homotris, a colorless solid: 3.4 g; bp 220–235 °C (0.5 mm); mp 108.5–109.8 °C; ^1H NMR (D_2O, dioxane: δ 3.70) δ 1.37 (s, $CH_2CH_2CH_2OH$, 12 H), 3.54 (t, CH_2OH, J = 5.4 Hz, 6 H); IR (Nujol mull) 3500–2900, 3330, 3287, 1620, 1224, 1064 cm^{-1}; ^{13}C NMR δ 61.7 (CH_2OH), 52.4 (CNH_2), 36.3 ($CH_2CH_2CH_2OH$), 26.8 (CH_2CH_2OH); MS, *m/e* 206 ($M^+ + H$, 1). Anal. Calcd for $C_{10}H_{23}NO_3$: C, 58.54; H, 11.22; N, 6.83. Found: C, 58.48; H, 11.12; N, 6.70.

4-Ammonio-4-[1-(3-chloropropyl)]-1,7-dichloroheptane Chloride (5). To bis-homotris (500 mg, 2.44 mmol) was added dropwise excess thionyl chloride.[29] The mixture was stirred at 25 °C for 10 min or until dissolution was complete. Excess $SOCl_2$

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was removed in vacuo to give (94%) the crude material, which was eluted through a short-path silica column with first CH_2Cl_2 followed by a 50:50 mixture of $EtOH/CH_2Cl_2$ to obtain (84%) **5**: 600 mg; mp >350 °C; ^1H NMR ($CDCl_3$) δ 1.91 (br s, CH_2C-H_2CH_2Cl, 12 H), 3.60 (br s, CH_2Cl, 6 H), 8.60 (broad s, NH_3, 3 H); IR (KBr) 3400–2575, 2959, 2039, 1518, 652 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 58.5 (H_3NC), 44.1 (CH_2Cl), 33.2 ($CH_2CH_2CH_2Cl$), 25.7 (CH_2CH_2Cl); MS, *m/e* 184 ($M^+ - C_3H_6Cl_2$, 65). Anal. Calcd for $C_{10}H_{21}Cl_4N$: C, 40.40; H, 6.06; N, 4.71. Found: C, 40.67; H, 6.28; N, 4.51.

1-Azoniatricyclo[3.3.3.0]undecane Chloride (6). To a mixture of acetonitrile (300 mL) and K_2CO_3 (2.5 g) was added the amine hydrochloride (**5**; 680 mg, 2.29 mmol). The stirred mixture was refluxed for 24 h; then after cooling to 25 °C, the K_2CO_3 was removed via filtration through a Celite pad. The filtrate was concentrated to yield (86%) azapropellane **6**: 370 mg. The crude material was chromatographed on a short alumina column, eluting with EtOH/EtOAc (50:50) to afford (74%) **6**: 320 mg; mp >350 °C; ^1H NMR (D_2O, dioxane: δ 3.70) δ 1.98 (br s, $CH_2CH_2CH_2N$, 12 H), 3.40 (m, CH_2N, 6 H); IR (KBr) 3470, 3300, 2970, 2100, 1458 cm^{-1}; ^{13}C NMR (CD_3CN: δ 117.7, 1.3) δ 79.2 (*C*N), 64.9, 64.7, 64.5 (CH_2N), 37.0 ($CH_2CH_2CH_2N$), 23.3 (CH_2CH_2N); MS, *m/e* 152 (M^+ - Cl, 9). Anal. Calcd for $C_{10}H_{18}ClN$: C, 64.00; H, 9.60; N, 7.47. Found: C, 63.91; H, 9.60; N, 7.60.

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Registry No. **1**, 116747-79-6; **2**, 1466-48-4; **3**, 59085-15-3; **4**, 116747-80-9; **5**, 116747-81-0; **6**, 116747-82-1; acrylonitrile, 107-13-1; nitromethane, 75-52-5.

A Novel Application of the Friedel–Crafts Reaction to the Synthesis of Differently Substituted Polynuclear Compounds

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The Friedel–Crafts reaction has been studied extensively for more than a century, and numerous compounds have been synthesized through alkylation, acylation, cycliacylation, and other miscellaneous types of reactions.[2,3] Most of the syntheses involve the use of stoichiometric amounts of the substrates, reactants, and the catalysts. Although the influence of temperature and excess amounts of the substrates, reactants, and catalysts in the orientation of alkylation and acylation of aromatic compounds has also been reported and Gore et al.[4-6] described diacylation of naphthalene derivatives by the use of excess amounts of acylating agents, we reported[7] for the first time that when excess amounts of substrates like anisole and phenetole are used, interesting polynuclear compounds are formed as secondary reaction products. Roberts et al.[8,9] also observed similar novelties subsequently. We also demonstrated that formation of the unexpected products depends on the nucleophilicity of the substrate and electrophilicity of the acyl carbonyl group of the initially formed acylated product.[10] In our attempt to synthesize differently substituted polynuclear compounds by the reaction of dichloroacetyl chloride and different pairs of substituted benzenes under Friedel–Crafts conditions, it was contemplated that the initially formed acylated product of one arene might react with the other nucleophile, if present in the reaction mixture, generating the desired compounds. With this aim in view, arenes with varying degrees of nucleophilicity were used as pairs of substrates and it was, indeed, observed that differently substituted polynuclear compounds of choice could conveniently be prepared by regulating the reaction conditions. We believe that our approach to this type of polynuclear compound is notable for its generality, preparative simplicity, and conceptual novelty.

Results and Discussion

The substrates used for the study were mono- and disubstituted benzenes of varying nucleophilicity, e.g., toluene, chlorobenzene, anisole, phenetole, *m*-xylene, and dimethylresorcinol. Initially the reaction was carried out under Friedel–Crafts conditions with the nucleophile of lower reactivity using stoichiometric proportions of the reactants and the catalyst to facilitate the formation of the normal acylated product. Application of higher temperature for stimulating the reaction was found to be necessary for the substrates of lower reactivity. No solvent was used for the initial acylation reaction as all the substrates used were liquids. However, for the reaction of the acylated product and the second substrate, CS_2 was used as solvent.

The normal acylated product of anisole formed initially by the reaction of stoichiometric amounts of anisole, dichloroacetyl chloride, and anhydrous $AlCl_3$ reacted in situ with a unimolar proportion of phenetole to yield 2,2-dichloro-1-(4′-ethoxyphenyl)-1-(4″-methoxyphenyl)ethylene (**1**) (Chart I). The same product could also be obtained by the reaction of the normal acylated product of phenetole on anisole. A minor byproduct characterized as 2,2-dichloro-1-(4′-ethoxyphenyl)-1-(4″-hydroxyphenyl)ethylene (**2**) was also formed, obviously by demethylation of the anisole part. Following a similar experimental protocol, we could also prepare the mixed dimeric products 2,2-dichloro-1-(4′-methoxyphenyl)-1-(2″,4″-dimethoxyphenyl)ethylene (**3**), 2,2-dichloro-1-(4′-methylphenyl)-1-(2″,4″-dimethoxyphenyl)ethylene (**4**), 2,2-dichloro-1-(4′-methylphenyl)-1-(4″-methoxyphenyl)ethylene (**5**), and 2,2-dichloro-1-(4′-chlorophenyl)-1-(4″-methoxyphenyl)-ethylene (**6**) by the use of anisole and dimethylresorcinol, toluene and dimethylresorcinol, toluene and anisole, and chlorobenzene and anisole respectively. The structures of these dimeric products were established by their elemental

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