This procedure was followed for the reduction of the other conjugated carbonyl compounds. The allylic alcohols obtained were purified (≥95%) by column chromatography (distillation was avoided to prevent loss of material due to decomposition or polymerization). The products were identified and the purities were checked by comparison with authentic samples (TLC, IR, and ^{1}H NMR).

Spectral data for 3-carbomethoxycyclohex-2-en-1-ol (entry 4): IR (neat) 3200–3500 (broad), 1715 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.2–2.3 (m, 6 H), 3.62 (s, 3 H), 3.84 (broad s, 1 H), 4.20 (broad, 1 H), 6.81 (m, 1 H) (homogeneous by GLC and TLC).

Reduction of 3-Methylcyclohex-2-en-1-one on a Multigram Scale. 3-Methylcyclohexenone (5.5 g, 0.05 mol) was added dropwise to a stirred suspension of $Zn(BH_4)_2$ (14.25 g, 0.15 mol) supported on silica gel (30 g; (prepared as in the previous text from the solution (140 mL) of $Zn(BH_4)_2$ in DME and silica gel) in THF (100 mL) under N_2 and stirred further for 8 h at −5 to −10 °C. The reaction was worked up as in the previous text and the crude product was chromatographed over silica gel to leave the pure alcohol (4.56 g, 80%).

Alternatively, supported reagent can be added in portions to the solution of 3-methylcyclohexenone in THF to get same result.

Reduction of Cyclohex-2-en-1-one with the Supported Reagent without Any Solvent. Neat cyclohexenone (96 mg, 1 mmol) was added to the solid supported reagent, prepared as in the previous text, at −78 °C under N_2, and stirring was continued for 8 h (monitored by TLC). The reaction mixture was decomposed with careful dropwise addition of H_2O and worked up as in the previous text to furnish pure cyclohex-2-en-1-ol (54 mg, 55%) after chromatography. The same procedure was followed for the reduction of cyclopentenone at −23 °C.

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Four-Directional Building Blocks for the Synthesis of Cascade Polymers[1]

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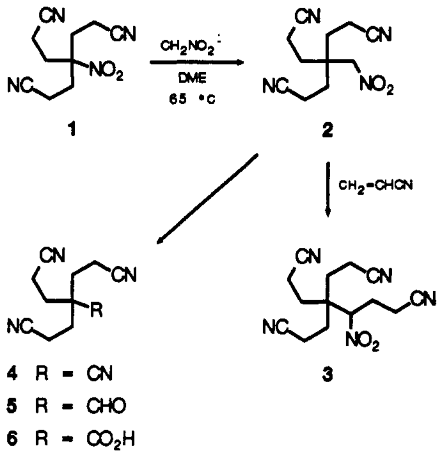
Tris(β-cyanoethyl)nitromethane (1) has become a convenient and inexpensive starting material for the construction of cascade polymers ("arborols")[2] and Micellanes.[3] Although transformations have been reported involving the nitrile functionality of 1, little attention has been given to the conversion of the nitro group into carboxylic acid derivatives.[4] Since nitro groups attached to tertiary carbon atoms can undergo radical anionic displacement reactions,[5] we decided to investigate the potential use of 1 as a source of new building blocks for cascade polymers.

Scheme I



Homologation was easily accomplished by treatment of the sodium salt of nitromethane with 1, thus providing a quaternary C-center having a $-CH_2NO_2$ substituent. Subsequent transformations of the $-CH_2NO_2$ moiety (Scheme I) gave rise to novel polyfunctionalized neopentane cores.

Although the reaction of 4 mol of nitromethyl anion with 1 mol of 1 in DMSO in the presence of an external light source did not occur at 25 °C,[5,6] reaction commenced spontaneously at 60–65 °C and was terminated after ~30 min, providing 2 in 64% yield. Extended reaction times caused diminished yields of isolated product. Compound 2 was easily characterized by the appearance of a new peak at δ 78.2 in the ^{13}C NMR spectrum for the CH_2NO_2 and a notable shift ($\Delta\delta$ 50) for the quaternary carbon. Interestingly, as noted earlier,[5] no reaction was observed when DMF was used as a solvent. Further substitution of 2 with acrylonitrile in the presence of Triton-B or DBU was restricted to the introduction of only one β-cyanoethyl group, affording 3 in 40% yield. The ^{13}C NMR spectrum of 3 shows a peak at δ 92.2 ($CHNO_2$) and other peaks for the unique cyanoethyl moiety. Presumably, steric factors hamper any further approach of a second acrylonitrile molecule. It should be noted that the generally facile replacement of the nitro group in 1 by a β-cyanoethyl moiety by using tri-*n*-butyltin hydride[7] failed completely.

Transformations of a primary nitro group into other functionalities have been reported.[8] Conversion of the $-CH_2NO_2$ moiety into nitrile 4 by reaction with PCl_3 in pyridine was straightforward.[9] The appearance of two $C{\equiv}N$ peaks in the ^{13}C NMR spectrum at δ 119.6 and 120.3 in an approximate 1:3 ratio confirmed the structure of 4. Aldehyde 5 was prepared in excellent yield by the oxidation of 2 with $KMnO_4$ in aqueous potassium tetraborate solution.[10,11] The structural assignment is supported by the new peak in the ^{13}C NMR spectrum at δ 204.6 for the

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aldehydic carbon. Oxidation of 2 with $KMnO_4$ in a water–ethyl acetate mixture also furnished 5; however, contamination with unreacted starting material was present. Oxidation of the nitronate salt of 2 with $KMnO_4$ furnished the corresponding carboxylic acid 6, the ^{13}C NMR spectrum of which shows a peak at δ 176.3 for the CO_2H.

Four-directional C-cores[12] with a variety of terminal functional groups may now be readily prepared, thus making tris(β-cyanoethyl)nitromethane a most attractive building block for cascade polymers.

Experimental Section

General Comments. All melting points were taken in capillary tubes and are uncorrected. The ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$, unless otherwise stated.

DMSO was dried and stored over 3A molecular sieves. Pyridine was dried over solid KOH, then distilled and stored over KOH. Unless specified, solvents were purified by simple distillation. Tris(β-cyanoethyl)nitromethane (Aldrich; 1, 1 g) was recrystallized from MeCN/EtOH (6 mL; 1:5): mp 114–116 °C.

3-(Nitromethyl)-3-(2-cyanoethyl)-1,5-dicyanopentane (2). Freshly distilled CH_3NO_2 (10 g, 160 mmol) was carefully added to a stirred slurry of NaH (3.92 g, 163 mmol; 95%) in dry DMSO (350 mL) under an inert atmosphere. After the foaming had subsided, a solution of tris(β-cyanoethyl)nitromethane (8.8 g, 40 mmol) in DMSO (50 mL) was added and the mixture was irradiated (100-W incandescent lamp). The temperature was allowed to rise to 65 °C within a period of 35 min and maintained at 65 °C for an additional 25 min. The yellow solution was then cooled to 25 °C, treated with AcOH (18 mL), and then poured into water (4 L). After the aqueous solution was extracted with EtOAc (7 × 100 mL), the combined organic fraction was washed with brine and dried ($MgSO_4$). The residue was chromatographed (SiO_2), eluting with $EtOAc/CH_2Cl_2$ (3:7), to give the homologue 2 as colorless crystals: yield, 6 g (64%); mp 100.5–102 °C (MeOH); ^1H NMR (DMSO-d_6) δ 1.18–1.77 (m, $CH_2CH_2C\equiv N$, 6 H), 1.99–2.68 (m, $CH_2C\equiv N$, 6 H), 4.64 (s, CH_2NO_2, 2 H); ^{13}C NMR δ 10.8 ($CH_2C\equiv N$), 28.3 ($CH_2CH_2C\equiv N$), 40.4 (quat C), 78.2 (CH_2NO_2), 120.4 ($C\equiv N$); IR (KBr) 2225 ($C\equiv N$), 1558, 1383 (NO_2) cm^{-1}. Anal. Calcd for $C_{11}H_{14}N_4O_2$: C, 56.39; H, 6.02; N, 23.91. Found: C, 56.43; H, 6.05; N, 23.99.

3,3-Bis(2-cyanoethyl)-4-nitro-1,6-dicyanohexane (3). To a solution of 2 (1.17 g, 5 mmol) and acrylonitrile (2.0 g, 37 mmol) in dimethoxyethane (DME; 20 mL) was added Triton-B (40% in water, 640 mg), and then the mixture was stirred at 25 °C for 48 h. Additional catalyst (650 mg) was added after 24 h. The catalyst was neutralized with dilute aqueous HCl, and the reaction mixture was concentrated in vacuo to afford a residue, which was stirred with EtOAc (50 mL) and water (10 mL). After the layers were separated, the combined organic phase was evaporated to dryness to give an oil. This was column chromatographed (SiO_2), eluting with $EtOAc/CH_2Cl_2$ (3:7) to furnish 3, as colorless crystals: yield, 580 mg (40%); mp 114–116 °C (MeOH); ^1H NMR δ 1.72–1.82 (m, $CH_2CH_2C\equiv N$, 6 H), 2.45–2.50 (m, $CH_2C\equiv N$, 6 H), 4.72 (m, $CHNO_2$, 2 H); ^{13}C NMR δ 11.5 (3 × $CH_2C\equiv N$), 14.08 ($CH_2C\equiv N$), 23.8 ($CH_2CH_2C\equiv N$), 28.5 (3 × $CH_2CH_2C\equiv N$), 41.4 (quat C), 92.2 ($HCNO_2$), 119.16 ($C\equiv N$), 120.3 (3 × $C\equiv N$); IR (KBr) 2260 ($C\equiv N$), 1558 (NO_2) cm^{-1}. Anal. Calcd for $C_{14}H_{17}N_5O_2$: C, 58.52; H, 5.96; N, 24.38. Found: C, 58.59; H, 6.02; N, 24.32.

3-(2-Cyanoethyl)-1,3,5-tricyanopentane (4). A solution of 2 (468 mg, 2 mmol), pyridine (5 mL), and PCl_3 (430 mg, 3 mmol) was maintained at 25 °C for 35 h, diluted with water (80 mL), and acidified with concentrated HCl (5 mL). The aqueous solution was extracted with EtOAc (3 × 50 mL), and the combined extract was dried ($MgSO_4$). Evaporation of the solvent afforded the tetranitrile as colorless crystals: yield, 270 mg (69%); mp 128–130 °C (MeOH); ^1H NMR β 1.16–1.73 (m, $CH_2CH_2C\equiv N$, 6 H), 2.01–2.69 (m, $CH_2C\equiv N$, 6 H); ^{13}C NMR δ 12.0 ($CH_2C\equiv N$), 29.4 ($CH_2CH_2C\equiv N$), 39.0 (quat C), 119.6 ($C\equiv N$), 120.3 (3 × $C\equiv N$); IR (KBr) 2260 ($C\equiv N$) cm^{-1}. Anal. Calcd for $C_{11}H_{12}N_4$: C, 65.97; H, 6.04; N, 27.98. Found: C, 65.80; H, 5.85; N, 28.11.

3-Formyl-3-(2-cyanoethyl)-1,5-dicyanopentane (5). A solution of 2 (468 mg, 2 mmol) in MeOH was added to LiOMe (80 mg, 2.1 mmol) in MeOH (15 mL) at 0 °C. After concentration in vacuo, the remaining salt was dissolved in saturated aqueous $K_2B_4O_7$ (25 mL). A solution of $KMnO_4$ (316 mg, 2 mmol) in saturated aqueous $K_2B_4O_7$ (25 mL) was added dropwise. After addition, the solution was stirred for an additional 30 min and then decolorized with aqueous $Na_2S_2O_4$ and dilute H_2SO_4. The solution was extracted with EtOAc (2 × 30 mL), and then the combined extract was washed with water (5 mL), dried ($MgSO_4$), and concentrated in vacuo to give aldehyde 5 as colorless crystals: yield, 330 mg (82%); mp 108–110 °C (MeOH); ^1H NMR δ 1.18–1.76 (m, $CH_2CH_2C\equiv N$, 6 H), 1.98–2.62 (m, $CH_2C\equiv N$, 6 H), 9.71 (s, CHO, 1 H); ^{13}C NMR δ 11.13 ($CH_2C\equiv N$), 25.9 ($CH_2CH_2C\equiv N$), 50.4 (quat C), 120.4 ($C\equiv N$), 204.6 (CHO); IR (KBr) 2823, 2726 (CH stretch), 2250 ($C\equiv N$), 1720 (CHO) cm^{-1}. Anal. Calcd for $C_{11}H_{13}N_3O$: C, 65.00; H, 6.45; N, 20.68. Found: C, 64.84; H, 6.52; N, 20.61.

2,2-Bis(2-cyanoethyl)-4-cyanobutanoic Acid (6). To a stirred solution of MeOLi (60 mg, 1.65 mmol) in water (20 mL) was added 2 (350 mg, 1.5 mmol) followed by aqueous $KMnO_4$ (340 mg, 2 mmol; 30 mL of H_2O). The MnO_2 was dissolved by adding $Na_2S_2O_4$ and dilute H_2SO_4. Repeated extraction with Et_2O (5 × 30 mL) then concentration in vacuo of the combined organic extract gave acid 6 as colorless crystals: yield, 250 mg (65%); mp 126–127 °C ($MeOH/H_2O$); ^1H NMR δ 1.18–1.77 (m, $CH_2CH_2C\equiv N$, 6 H), 1.97–2.63 (m, $CH_2C\equiv N$, 6 H); ^{13}C NMR δ 13.00 ($CH_2C\equiv N$), 29.96 ($CH_2CH_2C\equiv N$), 48.1 (quat C), 121.7 ($C\equiv N$), 176.3 (CO_2H); IR (KBr) 2260 ($C\equiv N$), 1705 (CO_2H) cm^{-1}. Anal. Calcd for $C_{11}H_{13}N_3O_2$: C, 60.25; H, 5.98; N, 19.17. Found: C, 60.26; H, 6.01; N, 19.30.

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Registry No. 1, 1466-48-4; 2, 133887-78-2; 3, 133909-48-5; 4, 133887-79-3; 5, 36394-40-8; 6, 133887-80-6; $CH_2{=}CHCN$, 107-13-1; nitromethane sodium salt, 25854-38-0.

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Chemistry of Cyclic Phosphorous Compounds. 4. Syntheses of the Sex Pheromone from the Pedal Gland of Bontebok and Some 1,4-Diketones by Use of 1,1-Diphenylphospholanium Perchlorate

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The Wittig reactions of the ylides generated from cyclic phosphonium salts afford the phosphine oxides[1] which have a newly formed carbon–carbon double bond. Further olefination of the phosphine oxides by the Horner–Wittig reaction results in the formation of a diene.[2] These tandem Wittig reactions with the same phosphorous atom from a cyclic phosphonium salt provide a versatile procedure for synthesis of unconjugated dienes. We have previously reported the synthesis of 1,6-dienes[3] by the

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