An Improved Synthesis of 2-Vinyl-4,5-dicyanoimidazole
and Characterization of its Polymers

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Supplement

4,5-dicyano-1-ethyl-2-vinylimidazole [1-ethylvinazene] (4b)

This compound was prepared in similar fashion to 4a, with diethylsulfate being
used as the appropriate electrophile, and resulting in 79% yield. However, longer
reaction periods were required, up to 5 days.

FW (calc'd) 172.18. mp 68-70°C (from ether/hexanes). TLC Rf 0.42 (50/50
hexanes/ethyl acetate). ¹H NMR (400 MHz, DMSO-d₆) δ (ppm) 6.93 (dd, 1H, α, J=16.9
Hz, 11.0 Hz), 6.35 (dd, 1H, β-trans, J=16.9 Hz, 1.5 Hz), 5.82 (dd, 1H, β-cis, J=11.0 Hz,
1.5 Hz), 4.27 (q, 2H, CH₂, J=7.3 Hz), 1.33 (t, 3H, Me, J=7.3 Hz). ¹³C NMR (100 MHz;
DMSO-d₆) δ (ppm) 149.21 (2), 125.33 (α), 121.42 (β), 120.92 (4), 112.48 (CN), 112.19
(CN), 108.81 (5), 41.59 (CH₂), 15.63 (Me). IR (KBr Pellet, cm⁻¹) 2235, 1911, 1623,
1525, 1489, 1447, 1433, 1377, 1342, 1321, 1300. LRMS (El/70 eV) m/z 344 (5, 2M⁺),
173 (85, M⁺+1), 172 (100, M⁺), 171 (12, M⁺-H), 157 (11, M⁺-Me), 144 (57, M⁺-C₂H₄),
143 (17, M⁺-Et), 49 (17), 39 (13). UV/Vis (CH₃CN) λ_max (ε) (nm, M⁻¹ cm⁻¹) 265
(13,600). Anal. calc'd for C₆H₆N₄: C, 62.8; H, 4.68; N, 32.5. Found: C, 63.0; H, 4.80; N,
32.6.

4,5-dicyano-1-dodecyl-2-vinylimidazole (4c)
This compound was prepared in similar fashion to 4a, with dodecyl bromide being used as the appropriate electrophile, and resulting in 18% yield. However, longer reaction periods were required, up to 13 days.

FW (calc’d) 312.46. mp 64-67°C (from ether/hexanes). TLC Rf 0.63 (50/50 hexanes/ethyl acetate). 1H NMR (400 MHz; CDCl3-d1) δ (ppm) 6.48 (m, 2H, α, β-trans), 5.78 (dd, 1H, β-cis, J=7.7 Hz, 4.4 Hz), 4.06 (t, 2H, J=7.3 Hz), 1.74 (m {poorly resolved triplet, J=6.9 Hz}, 2H), 1.24 (m, 18H), 0.82 (t, 3H, J=6.6 Hz). 13C NMR (100 MHz; CDCl3-d1) δ (ppm) 149.24 (2), 126.41 (α), 122.282 (4), 120.05 (β), 112.17 (CN), 111.72 (CN), 108.33 (5), 46.57 (α-CH2), 31.83 (CH2), 30.599 (CH2), 29.50 (CH2), 29.49 (CH2), 29.37 (CH2), 29.25 (CH2), 29.23 (CH2), 28.87 (CH2), 26.28 (CH2), 22.62 (CH2), 14.07 (CH3). IR (KBr Pellet, cm⁻¹) 2954, 2916, 2852, 2246, 2229, 1916, 1772, 1734, 1716, 1699, 1684, 1653, 1635, 1558, 1540, 1490, 1473, 1456, 1433, 1367, 1324. LRMS (EI/70 eV) m/z 312 (2, M⁺), 283 (5, M⁺-Et), 181 (6), 169 (8, C12H25⁺), 151 (18), 149 (16), 137 (88), 135 (90), 131 (12), 119 (12), 97 (10), 85.9 (8), 85.1 (29), 83.9 (13), 83.1 (21), 71 (48), 70 (11), 69 (47), 57 (94), 56 (18), 55 (65), 44 (17), 43 (100), 42 (15), 41 (68), 40 (23). UV/Vis (CH3CN) λmax (ε) (nm, M⁻¹ cm⁻¹) 265 (35,700). Anal. calc’d for C14H10N4: C, 73.0; H, 9.03; N, 17.9. Found: C, 72.9; H, 9.19; N, 17.7.

1-benzyl-4,5-dicyano-2-vinylimidazole (4d)³

This compound was prepared in similar fashion to 4a, with benzyl chloride/KBr being used as the appropriate electrophile resulting in 64% yield. However, longer reaction periods were required, up to 15 days.

FW (calc’d) 234.26. mp 123-125°C (from ether/hexanes). TLC Rf 0.65 (50/50 hexanes/ethyl acetate). 1H NMR (400 MHz; DMSO-d6) δ (ppm) 7.36 (m, 3H, Ph), 7.18 (m, 2H, Ph), 6.94 (dd, 1H, α, J=16.9 Hz, 11.0 Hz), 6.35 (dd, 1H, β-trans, J=16.9 Hz, 1.5 Hz), 5.81 (dd, 1H, β-cis, J=11.0 Hz, 1.5 Hz), 5.52 (s, 2H). 1H NMR (400 MHz; CDCl3-d1) δ (ppm) 7.38 (m, 3H, Ph), 7.12 (m, 2H, Ph), 6.52 (m, 2H, α, β-trans), 5.78 (dd, 1H, β-cis, J=9.2 Hz, 3.3 Hz), 5.28 (s, 2H). 13C NMR (100 MHz; CDCl3-d1) δ (ppm) 149.67 (2), 132.97 (Ph), 129.57 (Ph), 129.31 (Ph), 126.94 (α), 126.82 (Ph), 120.22 (B), 111.58 (CN), 108.33 (5), 49.73 (CH2). IR (KBr Pellet, cm⁻¹) 2242, 2248, 1496, 1461, 1426, 1371, 1342, 1314, 1300. LRMS (EI/70 eV) m/z 234 (11, M⁺), 91 (100, PhCH2⁺), 65 (17).
UV/Vis (CH₃CN) λ_{max} (ε) (nm, M⁻¹ cm⁻¹) 266 (27,800). Anal. calc'd for C₁₄H₁₀N₄: C, 71.8; H, 4.30; N, 23.9. Found: C, 72.0; H, 4.57; N, 23.7.

4,5-dicyano-1-methyl-2-(2-pyrrolidinylethyl)imidazole (5b)

In a test tube, 1-methylvinazene, 200 mg (1.3 mmol), was dissolved in 1 mL of DMSO with stirring, and pyrrolidine, 1 mL (5.6 mmol), was added. After 1 hour, the mixture was diluted with water, 40 mL, and extracted with 4-20-mL portions of ethyl acetate. The combined organic layers were evaporated under reduced pressure. The residual oil resisted all attempts at crystallization, and the smell of pyrrolidine persisted indefinitely. The crude ¹H NMR clearly showed the presence of the product as evidenced by the α,β coupling pattern, which was very similar to the morpholine adduct of 1-methylvinazene. Upon standing for 6 months, the 1-methylvinazene starting material crystallized; no further work was done to isolate this compound.

FW (calc'd) 217.28. TLC Rf 0 (50/50 hexanes/ethyl acetate). ¹H NMR (300 MHz; DMSO-𝑑₆) δ (ppm) 3.76 (s, 2H), 2.94 (m {poorly resolved triplet}, 2H), 2.76 (m {poorly resolved triplet}, 2H) 2.49 (m, overlapping with solvent peak), 1.67 (m, 4H). IR (KBr Pellet, cm⁻¹) 2994, 2242, 1911, 1679, 1525, 1489, 1440, 1377, 1342, 1321.

4,5-dicyano-1-methyl-2-(2-phenylthioethyl)imidazole (5c)

In a test tube, 4,5-dicyano-2-vinyl-1-methylimidazole, 0.15 g (0.95 mmol) was dissolved in thiophenol, 2 mL (15 mmol), and methanol, 5 mL, with stirring; to this mixture, 3 drops of triethylamine were added. The reagents were allowed to stir overnight. The mixture was taken up in 150 mL of ethyl acetate and washed with 3 40-mL portions of 10% aqueous sodium hydroxide. The combined organic layers were dried with magnesium sulfate and evaporated under reduced pressure. The residue was dry-loaded onto a 1" plug of neutral activated alumina. This plug was eluted with 300 mL of 10% ethyl acetate in hexanes. Subsequent to the ethyl acetate/hexanes elution, 150 mL of acetone was eluted through the column. The acetone was allowed to air-dry and the residue recrystallized in acetone/hexanes to yield 0.14 g (55%) of yellow platelets in one crop.

FW (calc'd) 268.34. mp 104-108°C (from acetone/hexanes). TLC Rf 0.36 (50/50 hexanes/ethyl acetate). ¹H NMR (400 MHz; DMSO-𝑑₆) δ (ppm) 7.34 (m, 4H, Ph), 7.22 (m, 4H, Ph), 3.70 (s, 3H, Me), 3.36 (t, 2H, β, J=7.0 Hz), 2.99 (t, 2H, α, J=7.0 Hz). ¹³C
NMR (100 MHz; DMSO-$d_6$) δ (ppm) 152.92 (2), 135.03 (Ph-ipso), 129.07 (Ph-para), 128.51 (Ph-ortho), 126.06 (Ph-meta), 119.38 (4), 113.07 (CN), 112.49 (CN), 108.76 (5), 33.00 (Me), 29.48 (β), 26.69 (α). IR (KBr Pellet, cm$^{-1}$) 2235, 1581, 1510, 1468, 1440, 1426, 1419, 1412, 1321. LRMS (EI/70 eV) m/z 269 (10, M$^+1$), 268 (43, M$^+$), 222 (12), 218 (15), 159 (23, M$^+$-PhS), 146 (33, M$^+$-PhSCH$_2$), 124 (10), 123 (100, PhSCH$_2$), 110 (15), 109 (30, PhS$^+$) 79 (11), 77 (26.09, Ph$^+$). UV/Vis (CH$_3$CN) λ$_{max}$ (ε) (nm, M$^{-1}$ cm$^{-1}$) 257 (31,800), 269 (24,500), 278 (13,800). Anal. calc'd for C$_{14}$H$_{10}$N$_4$: C, 62.7; H, 4.51; N, 20.9. Found: C, 63.5; H, 4.61; N, 20.9. HRMS 268.0783 (calc'd for C$_{14}$H$_{12}$N$_4$S: 268.0783).

4-(4,5-dicyano-2-imidazoly) bicyclo[2.2.1]hept-2-ene (7a)

To a test-tube fitted with a magnetic stirrer, 253 mg (1.8 mmol) of vinazene, 2 mL of ether, 2mL (24 mmol) of freshly cracked cyclopentadiene, and 100 mg (2.4 mmol) of lithium chloride were added. After stirring for 1 day, the solution was washed with 3-2 mL portions of water. The aqueous phase was back-extracted with 3-2 mL portions of ether. The combined ether solutions were dried with sodium sulfate and evaporated under reduced pressure. The remaining residue was washed with several portions of hexanes and allowed to air-dry, yielding 336 mg (91%). Crystallization with ether/hexanes or ethanol water failed. Analysis of the crude mixture via NMR and MS shows presence of desired products in a 3:1 ratio of diastereomers.

FW (calc’d) 210.24. TLC Rf TLC R$_f$ 0.51 (major isomer), 0.61 (minor isomer); (50/50 hexanes/ethyl acetate). $^1$H NMR (300 MHz; CDCl$_3$) δ (ppm) 6.20 (dd, 1H, J=5.5, 2.8 Hz, alkene trans to imidazole), 5.72 (dd, 1H, J=5.5, 2.8 Hz alkene cis to imidazole), 3.44 (dt, 1H, J=9.3, 4.1 Hz, overlapping residual water peak, α to imidazole), 3.26 (m, 1H, overlapping residual water peak, bridgehead cis to imidazole), 2.94 (m, 1H, bridgehead trans to imidazole), 2.11 (m, 1H non-bridgehead, β-equatorial to imidazole), 1.40 (m, 3H, overlapping peaks including short bridge and β-axial to imidazole); additional minor product peaks, 2.99 (m), 2.68 (m), 2.58 (m), 2.06 (m) [These peaks assigned by analogy to the EtVz/Cp Diels-Alder Adduct, for which COSY, HSQC and NOESY information was available]. $^{13}$C NMR (100 MHz; CDCl$_3$) δ (ppm) 157.10 (2), 138.07 (alkene trans to imidazole), 132.15 (alkene cis to imidazole), 49.08 (bridgehead cis to imidazole), 46.56 (bridgehead trans to imidazole), 42.19 (α to imidazole), 37.30 (non-
bridgehead β to imidazole), 30.34; additional minor product peaks, 135.62 (alkene) 47.65 (bridgehead cis to imidazole), 41.34 (α to imidazole), 37.41 (non-bridgehead β to imidazole), 31.31; [These peaks assigned by analogy to the EtVz/Cp Diels-Alder Adduct, for which COSY, HSQC and NOESY information was available]. LRMS (EI/70 eV) m/z 210 (13, M⁺), 145 (22, M⁺-C₃H₅), 66 (100, C₃H₆⁺), 58 (24), 43 (66). HRMS 210.0909 (calc’d for C₁₃H₁₀N₄: 210.0905).

4- (4,5-dicyano-1-methyl-2-imidazoly) bicyclo[2.2.1]hept-2-ene (7b)

To a test-tube fitted with a magnetic stir bar, 252 mg (1.6 mmol) of 1-methylvinazene, 2 mL of ether, 2 mL (24 mmol) of freshly cracked cyclopentadiene, and 100 mg (2.4 mmol) of lithium chloride were added. After stirring for 1 day, the solution was washed with 3-2 mL portions of water. The aqueous phase was back-extracted with 3-2 mL portions of ether. The combined ether solutions were dried with sodium sulfate and evaporated under reduced pressure. The remaining residue was recrystallized with ether/hexanes. Following recrystallization, the product was washed with generous portions of cold hexanes and dried to yield 176 mg of product; NMR indicates this product to be a 2:1 mixture of diastereomers, endo:exo. An additional 219 mg of residue was present after concentrating the mother liquors, which NMR showed to be approximately 50% cyclopentadiene and 50% a 5:1 mixture of diastereomers, endo:exo.

FW (calc’d) 224.27. mp 116-118°C (from ether/hexanes). TLC Rf 0.40 (major isomer), 0.45 (minor isomer); (50/50 hexanes/ethyl acetate). ¹H NMR (400 MHz; CDCl₃) δ (ppm) 6.25 (m, 1H, alkene, trans to imidazole), 5.78 (m, 1H, alkene cis to imidazole), 3.78 (s, 3H, N-Me), 3.24 (m, 2H, two signals overlapped, α to imidazole and bridge head cis to imidazole), 3.01 (m, 1H, bridge head trans to imidazole), 2.16 (m, 1H, non-bridgehead, β-equatorial to imidazole), 1.58 (m, 2H, overlapping residual water peak, including short bridge, and, β-axial to imidazole), 1.42 (m, 1H (short bridge); additional minor product peaks, 6.18 (m), 3.75 (s, N-Me), 2.58 (m), 2.06 (m) [These peaks assigned by analogy to the EtVz/Cp Diels-Alder Adduct, for which COSY, HSQC and NOESY information was available]. ¹³C NMR (75 MHz; CDCl₃) δ (ppm) 156.39 (2), 137.89 (alkene trans to imidazole), 131.65 (alkene cis to imidazole), 111.94 (CN), 108.39 (5), 49.85 (bridgehead cis to imidazole), 46.31 (bridgehead trans to imidazole), 42.60 (α to imidazole), 36.76 (1-Me), 36.62 (non-bridgehead β to imidazole), 32.72,
31.37; additional minor product peak, 138.86 (alkene); [These peaks assigned by analogy to the EtVz/Cp Diels-Alder Adduct, for which COSY, HSQC and NOESY information was available]. IR (KBr Pellet, cm⁻¹) 3072, 2985, 2937, 2873, 2236, 1499, 1457, 1394, 1363, 1336, 1319. LRMS (EI/70 eV) m/z 224 (39, M⁺), 159 (84, M⁺-C₅H₅), 157 (14), 146 (28), 84 (16), 66 (100, C₆H₆⁺). UV/Vis (CH₃CN) λ_max (ε) (nm, M⁻¹ cm⁻¹) 262 (13,900). Anal. calc'd for C₈H₈N₄: C, 69.6; H, 5.4; N, 25.0. Found: C, 69.5; H, 5.5; N, 24.8.

4- (4,5-dicyano-1-ethyl-2-imidazolyl)bicyclo[2.2.1]hept-2-ene (7c)

To a test-tube fitted with a magnetic stir bar, 250 mg (1.45 mmol) of 1-ethylvinazene, 2 mL of ether, 2mL (24 mmol) of freshly cracked cyclopentadiene, and 100 mg (2.4 mmol) of lithium chloride were added. After stirring for 1 day, the solution was washed with 3-2 mL portions of water. The aqueous phase was back-extracted with 3-2 mL portions of ether. The combined ether solutions were dried with sodium sulfate and evaporated under reduced pressure. The oily residue was triturated with hexanes, and the precipitate was washed with generous portions of hexanes. The residue massed 257 mg, and was recrystallized with ether/hexanes. Following recrystallization the product was washed with generous portions of cold hexanes and dried to yield 184 mg of product. An additional 25 mg of residue was present after concentrating the mother liquors. COSY, HSQC and NOESY analysis indicates a >19:1 ratio of endo:exo.

FW (calc'd) 238.29. mp 97-99°C (from ether/hexanes). TLC Rf 0.41 (major isomer), 0.48 (minor isomer); (50/50 hexanes/ethyl acetate). ¹H NMR (500 MHz; CDCl₃) δ (ppm) 6.26 (dd, 1H, alkene trans to imidazole, J=5.8 Hz, 3.0 Hz), 5.79 (dd, 1H, alkene cis to imidazole, J=5.8 Hz, 2.8 Hz), 4.17 (q, 2H, N-CH₂, J=7.4 Hz), 3.26 (m, 1H, α to imidazole), 3.20 (m, 1H, bridge head cis to imidazole), 3.01 (m, 1H, bridge head trans to imidazole), 2.17 (ddd, 1H, J=11.5 Hz, 7.7 Hz, 2.2 Hz, non-bridgehead, β-equatorial to imidazole), 1.5 (m, 6H, several overlapping peaks; overlapping residual water peak, including methyl, short bridge, and, β-axial to imidazole). ¹³C NMR (100 MHz; CDCl₃) δ (ppm) 155.80 (2), 138.00 (alkene trans to imidazole), 131.67 (alkene cis to imidazole), 108.51 (CN), 58.03 (short bridge), 49.90 (bridgehead trans to imidazole), 47.09 (bridgehead cis to imidazole), 42.60 (α to imidazole), 41.36 (CH₂), 36.46 (non-bridgehead β to imidazole), 31.71, 16.00 (Me). IR (KBr Pellet, cm⁻¹) 3059, 2983, 2946,
2914, 2870, 2237, 1496, 1476, 1456, 1422, 1384, 1376, 1340, 1316, 1306. LRMS (EI/70 eV) m/z 238, (29, M'), 173 (52, M'-C₃H₅), 160 (20), 145 (17), 66 (100, C₆H₆⁺). UV/Vis (CH₃CN) λₘₚₓ (ε) (nm, M⁻¹ cm⁻¹) 267 (35,800). Anal. calc'd for C₉H₇N₄: C, 70.6; H, 5.9; N, 23.5. Found: C, 70.5; H, 6.0; N, 23.4.
Scheme 2

Supplement
Scheme 3

Supplement