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Convenient synthesis of polycationic amphiphiles by the Fukuyama reaction

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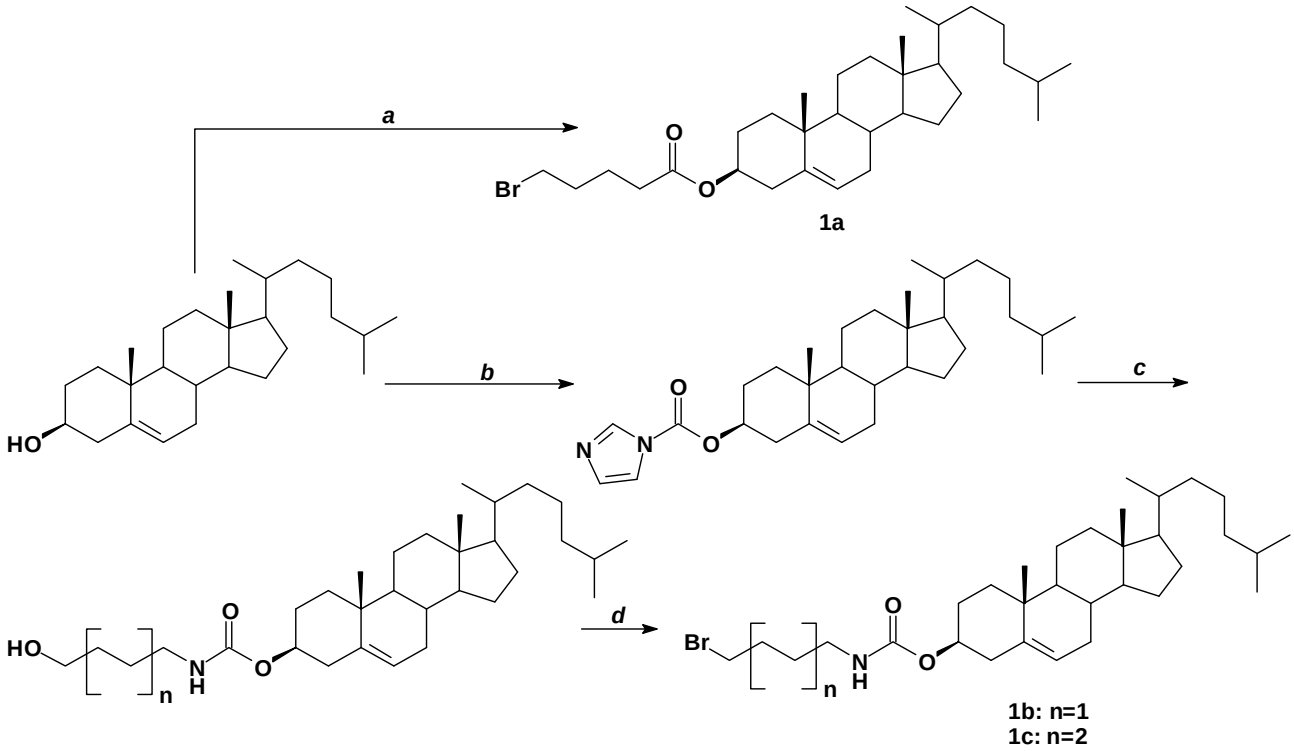

(*a*) $Br(CH_2)_4C(O)Cl$, Py, 24 ºC, 96%; (*b*) CDI, Et_3N, 40 ºC, 99%; (*c*) 4-aminobutanol or 6-aminohexanol, 40ºC, 87% (90%); (*d*) CBr_4, Ph_3P, 24 ºC, 84% (84%).

Cholest-5-en-3β-yl 5-bromopentanoate 1a: mp 112-114 °C. ^{1}H NMR, δ: 0.68 (s, 3 H, 18-CH_3), 0.79 (d, 3 H, J = 6.5, 27-CH_3), 0.80 (d, 3 H, J = 6.5, 26-CH_3), 0.86 (d, 3 H, J = 6.5, 21-CH_3), 1.02 (s, 3 H, 19-CH_3), 0.88-1.65 (m, 26 H, Chol, $OOCCH_2(CH_2)_2$), 1.68-2.00 (m, 7 H, Chol), 2.13-2.34 (m, 2 H, 4-CH_2), 3.06-3.19 (m, 2 H, CH_2COO), 3.40 (т, 2 H, J = 6.7, CH_2Br), 4.34-4.49 (m, 1 H, 3-H), 5.27-5.34 (m, 1 H, 6-H).

Cholest-5-en-3β-yl 1*H*-imidazole-1-carboxylate: mp 124-126 °C. ^{1}H NMR, δ: 0.61 (s, 3 H, 18-CH_3), 0.79 (d, 3 H, J = 6.5, 27-CH_3), 0.80 (d, 3 H, J = 6.5, 26-CH_3), 0.84 (d, 3 H, J = 6.5, 21-CH_3), 0.99 (s, 3 H, 19-CH_3), 0.90-1.58 (m, 22 H, Chol), 1.58-2.02 (m, 7 H, Chol), 2.38-2.47 (m, 2 H, 4-CH_2), 4.69-4.83 (m, 1 H, 3-H), 5.34-5.40 (m, 1 H, 6-H), 7.00 (s, 1 H), 7.36 (s, 1 H), 8.09 (s, 1 H Im). ^{13}C NMR, δ: 11.88, 18.88, 19.35, 21.21, 22.63, 22.87, 23.98, 24.44, 27.81, 28.19, 28.38, 31.98, 35.96, 36.33, 36.71,

36.92, 38.03, 39.67, 39.83, 42.47, 50.11, 56.27, 56.81, 79.20, 117.44, 123.95, 130.05, 137.14, 138.74, 148.05

Cholest-5-en-3β-yl (4-hydroxybutyl)carbamate: mp 154-156 °C. mass *m/z* $[M+Na]^+$ 524.314. ^{1}H NMR, *δ*: 0.61 (s, 3 H, 18-CH_3), 0.79 (d, 3 H, *J* = 6.5, 27-CH_3), 0.80 (d, 3 H, *J* = 6.5, 26-CH_3), 0.85 (d, 3 H, *J* = 6.5, 21-CH_3), 0.94 (s, 3 H, 19-CH_3), 0.98-1.57 (m, 23 H, Chol, $NHCH_2(CH_2)_2$), 1.68-2.02 (m, 7 H, Chol), 2.14-2.38 (m, 2 H, 4-CH_2), 3.05-3.20 (m, 2 H, CH_2N), 3.59 (t, 2 H, *J* = 5.9, CH_2OH), 4.36-4.48 (m, 1 H, 3-H), 4.48-4.62 (m, 1 H, NH), 5.27-5.35 (m, 1 H, 6-H). ^{13}C NMR, *δ*: 12.10, 18.99, 19.56, 21.14, 22.79, 23.07, 23.93, 24.38, 26.54, 28.12, 28.26, 29.64, 31.96, 35.91, 36.27, 36.65, 37.06, 38.65, 39.61, 39.82, 40.70, 42.40, 49.94, 56.21, 56.77, 62.10, 74.57, 122.63, 139.89, 156.72.

Cholest-5-en-3β-yl (6-hydroxyhexyl)carbamate: mp 186-188 °C. ^{1}H NMR, *δ*: 0.61 (s, 3 H, 18-CH_3), 0.79 (d, 3 H, *J* = 6.5, 27-CH_3), 0.80 (d, 3 H, *J* = 6.5, 26-CH_3), 0.85 (d, 3 H, *J* = 6.5, 21-CH_3), 0.94 (s, 3 H, 19-CH_3), 0.98-1.57 (m, 27 H, Chol, $NHCH_2(CH_2)_4$), 1.68-2.00 (m, 7 H, Chol), 2.13-2.35 (m, 2 H, 4-CH_2), 3.03-3.16 (m, 2 H, CH_2N), 3.57 (t, 2 H, *J* = 6.4, CH_2O), 4.34-4.49 (m, 1 H, 3-H), 5.27-5.34 (m, 1 H, 6-H). ^{13}C NMR, *δ*: 12.03, 18.89, 19.51, 21.21, 22.73, 22.99, 24.00, 24.46, 25.48, 26.57, 28.19, 28.35, 28.41, 30.19 , 32.06, 35.97, 36.36, 36.73, 37.17, 38.76, 39.69, 39.91, 40.87, 42.49, 50.18, 56.30, 56.86, 62.90, 74.39, 122.64, 140.03, 156.40.

Cholest-5-en-3β-yl (4-bromoxybutyl)carbamate 1b: mp 92-94 ºC. ^{1}H NMR, *δ*: 0.61 (s, 3 H, CH_3-18), 0.79 (d, 3 H, *J* = 6.5, 27-CH_3), 0.80 (d, 3 H, *J* = 6.5, 26-CH_3), 0.85 (d, 3 H, *J* = 6.5, 21-CH_3), 0.94 (s, 3 H, 19-CH_3), 0.98-1.57 (m, 23 H, Chol, $NHCH_2(CH_2)_2$), 1.70-2.00 (m, 7 H, Chol), 2.15-2.38 (m, 2 H, 4-CH_2), 3.05-3.16 (m, 2 H, CH_2N), 3.35 (t, 2 H, *J* = 6.5, CH_2Br), 4.36-4.48 (m, 1 H, H-3), 4.48-4.62 (m, 1 H, NH), 5.27-5.34 (m, 1 H, H-6). ^{13}C NMR, *δ*: 12.17, 18.74, 19.37, 21.20, 22.87, 23.14, 24.00, 24.44, 28.18, 28.33, 28.90, 30.00, 32.02, 33.43, 35.97, 36.33, 36.71, 37.12, 38.72, 39.67, 39.88, 40.12, 42.46, 50.02, 56.27, 56.83, 74.48, 122.69, 139.93, 156.34.

Cholest-5-en-3β-yl (6-bromohexyl)carbamate 1c: mp 106-108 ºC. ^{1}H NMR, *δ*: 0.61 (s, 3 H, 18-CH_3), 0.79 (d, 3 H, *J* = 6.5, 27-CH_3), 0.80 (d, 3 H, *J* = 6.5, 26-CH_3), 0.85 (d, 3 H, *J* = 6.5, 21-CH_3), 0.94 (s, 3 H, 19-CH_3), 0.98-1.57 (m, 28 H, Chol, $NHCH_2(CH_2)_4$), 1.68-1.98 (m, 7 H, Chol), 2.12-2.34 (m, 2 H, 4-CH_2), 3.03-3.15 (m, 2 H, CH_2N), 3.34 (t, 2 H, *J* = 6.8, CH_2Br), 4.35-4.48 (m, 1 H, 3-H), 4.48-4.62 (m, 1 H, NH), 5.28-5.33 (m, 1 H, 6-H). ^{13}C NMR, *δ*: 12.04, 18.90, 19.52, 21.23, 22.74, 23.00, 24.01, 24.47, 26.08, 27.99, 28.19, 28.37, 28.42, 30.08, 32.07 32.81, 33.91, 35.98, 36.37, 36.75, 37.18, 38.76, 39.70, 39.92, 40.94, 42.50, 50.20, 56.32, 56.87, 74.40, 122.66, 140.03, 156.35.