

CHAPTER II

EXPERIMENTAL

General methods

NMR spectra were recorded in CDCl_3 solution on a Bruker instrument (SAG CH-8117) at 200 MHz (^1H) or at 50 MHz (^{13}C). Chemical shifts are given in parts per million (ppm) downfield from tetramethylsilane as an internal standard and coupling constants (J) are in Hz. Infrared spectra were obtained on an FT-IR spectrometer. Mass spectra were determined using a Fisons model Trio-200 GC-MS. Elemental analyses were carried out on a Perkin Elmer Elemental Analyzer 2400 CHN. The thermal properties were measured on a Netzsch Simultaneous Thermal Analyzer (STA 409 C) and a Perkin Elmer Differential Scanning Calorimeter (DSC 7). All reactions were followed by TLC : plastic sheets coated with silica gel 60 F_{254} (Merck). Flash chromatography was carried out on silica gel : 230-400 Mesh. Chemicals were obtained from Aldrich, Fluka and Merck and were used as received.

Preparation of Bis-(3-allyloxy-2-hydroxy-1-propoxy)diphenoxyp propane (3)

A mixture of bisphenol-A (**1**) (0.243 g, 1.16 mmol), allyl glycidyl ether (**2**) (0.251 g, 2.20 mmol) and sodium hydroxide (0.045 g, 1.12 mmol) was heated and stirred at 120°C for 3 hours, then taken up in ethyl acetate and washed with water. The organic layer was dried (MgSO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with 5% ethyl acetate/hexane to give (**3**) (0.452 g, 93% based on (**1**)) as a yellow liquid; ^1H NMR 7.13 (4H, d, $J=8.8$, H12), 6.81 (4H, d, $J=8.8$, H11), 5.82 (2H, tdd, $J=5.7$, $J=11.2$, $J=17.2$, H3), 5.30 (2H, tdd, $J=1.6$, $J=3.2$, $J=17.2$, H2), 5.16(2H, tdd, $J=1.6$, $J=3.3$, $J=11.5$, H1), 4.09-4.18 (2H, m, H8), 3.97-4.04 (8H, m, H4, H5, H9, H10), 3.61 (2H, dd, $J=4.4$, $J=9.6$, H6), 3.57 (2H, dd, $J=5.7$, $J=9.6$, H7), 1.61 (6H, s, H13); ^{13}C NMR 156.4 (C7), 143.5 (C10), 134.4 (C2), 127.8 (C9), 117.4 (C1), 113.9 (C8), 72.4 (C4), 70.9 (C6), 69.1 (C5), 68.9 (C3),

41.7 (C11), 31.0 (C12); ir/cm⁻¹ 3421 (OH), 3078, 2965, 1613, 1520, 1467, 1450, 1419, 1183, 1086, 1040, 932, 830; m/z 456 (M⁺), 441 (M⁺-CH₃), 399 (M⁺-C₃H₅O), 327 (M⁺-CH₃-C₆H₁₀O₂), 213 (M⁺-CH₃-2(C₆H₁₀O₂), 41 (CH₂=CH-CH₂⁺), 115 (CH₂=CHCH₂OCH₂CH(OH)CH₂⁺).

Analysis calc. for C₂₇H₃₆O₆: C 71.03; H 7.95, found: C 71.13; H 7.94.

Preparation of Bis-[3-(4-allyloxy-2-methoxy)phenoxy-2-hydroxy-1-propoxy]diphenoxyp propane (7)

A mixture of the diglycidyl ether of bisphenol-A (**6**) (0.264 g, 0.75 mmol), eugenol (**5**) (0.256 g, 1.56 mmol) and sodium hydroxide (0.064 g, 1.61 mmol) was heated and stirred at 120°C for 5 hours, then taken up in ethyl acetate and washed with water. The organic layer was dried (MgSO₄) and concentrated under reduced pressure. The residue was chromatographed on a silica gel column using 20% ethyl acetate/hexane as eluent to give (**7**) (0.322 g, 62% based on (**5**)) as a viscous yellow liquid ; ¹H NMR 7.13 (4H, d, J=8.8, H16), 6.68-6.89 (6H, m, H6, H7, H8), 6.83 (4H, d, J=8.8, H15), 5.87 (2H, tdd, J=6.6, J=11.4, J=16.8, H3), 5.11 (2H, tdd, J=1.6, J=3.3, J=17.1, H2), 5.02 (2H, tdd, J=1.4, J=3.3, J=11.1, H1), 4.29-4.37 (2H, m, H12), 4.08-4.21 (8H, m, H10, H11, H13, H14), 3.82 (6H, s, H9), 3.34 (4H, d, J=6.6, H4, H5), 1.60 (6H, s, H17) ; ¹³C NMR 156.4 (C14), 149.8 (C7), 146.4 (C6), 143.6 (C17), 137.5 (C2), 134.2 (C4), 127.8 (C16), 120.8 (C5), 115.8 (C1), 115.4 (C15), 113.9 (C8), 112.4 (C9), 71.6 (C13), 68.7 (C12), 68.6 (C11), 55.8 (C10), 41.7 (C18), 39.8, 31.0 ; ir/cm⁻¹ 3487 (OH), 3027, 2965, 1639, 1608, 1507, 1470, 1219, 1034, 927, 753 ; m/z 504 (M⁺-C₁₀H₁₂O₂), 489 (M⁺-CH₃-C₁₀H₁₂O₂), 340 (M⁺-2C₁₀H₁₂O₂), 164 (C₁₀H₁₂O₂), 41(CH₂=CH-CH₂⁺).

Analysis calc. for C₄₁H₄₈O₈ : C 73.63; H 7.23, found : C 73.66; H 7.33.

Preparation of 2,7-Bis-(3-allyloxy-2-hydroxy-1-propoxy)naphthalene (9)

A mixture of 2,7-dihydroxynaphthalene (**8**) (0.214 g, 1.34 mmol), allyl glycidyl ether (**2**) 0.310 g, 2.72 mmol) and sodium hydroxide (0.116 g, 2.90 mmol) was heated and stirred at 120°C for 5 hours, the taken up in ethyl acetate and washed with water.

The organic layer was dried (MgSO_4) and concentrated under reduced pressure. The residue was chromatographed on a silica gel column using 15% ethyl acetate/hexane as eluent to give (9). (0.401 g, 77% based on (8)) as a yellow liquid ; ^1H NMR 7.61 (2H, d, $J=8.6$, H12), 7.04 (2H, s, H11), 6.98 (2H, d, $J=8.8$, H13), 5.84 (2H, tdd, $J=5.7$, $J=10.6$, $J=16.1$, H3), 5.33 (2H, tdd, $J=1.5$, $J=3.2$, $J=17.2$, H2), 5.18 (2H, tdd, $J=1.7$, $J=3.3$, $J=13.7$, H1), 4.04-4.24 (10H, m, H4, H5, H8, H9, H10), 3.65 (2H, dd, $J=4.5$, $J=9.6$, H6), 3.64 (2H, dd, $J=5.6$, $J=9.6$, H7) ; ^{13}C NMR 157.2 (C7), 135.7 (C9), 134.4 (C2), 129.2 (C11), 124.6 (C10), 117.5 (C1), 116.3 (C8), 106.4 (C12), 72.4 (C4), 71.1 (C6), 69.1 (C3), 69.0 (C5) ; ir/cm⁻¹ 3424 (OH), 3074, 2929, 1633, 1513, 1447, 1420, 1454, 1040, 938, 844 ; m/z 388 (M^+), 274 ($\text{M}^+ - \text{C}_6\text{H}_{10}\text{O}_2$), 160 ($\text{M}^+ - 2\text{C}_6\text{H}_{10}\text{O}_2$), 160 ($\text{C}_{10}\text{H}_8\text{O}_2$), 115 ($\text{CH}_2 = \text{CHCH}_2\text{OCH}_2\text{CH(OH)CH}_2^+$), 57 ($\text{CH}_2 = \text{CHCH}_2\text{O}^+$), 41 ($\text{CH}_2 = \text{CHCH}_2^+$).

Analysis calc. for $\text{C}_{22}\text{H}_{28}\text{O}_6$: C 68.02; H 7.27 , found : C 68.04; H 7.36.

Preparation of Bis-(3-N,N-diallylamino-2-hydroxy-1-propoxy) diphenoxypy propane (11)

A mixture of the diglycidyl ether of bisphenol-A (6) (0.301 g, 0.91 mmol) and diallylamine (10) (0.187 g, 1.93 mmol) was heated and stirred at 80°C for 2 hours. The reaction mixture was purified by flash chromatography using 20% ethyl acetate/hexane as eluent to give (11) (0.422 g, 89% based on (10)) as a yellow liquid ; ^1H NMR 7.12 (4H, d, $J=8.9$, H12), 6.81 (4H, d, $J=8.9$, H11), 5.80 (4H, tdd, $J=5.9$, $J=10.9$, $J=17.3$, H3), 5.20 (4H, tdd, $J=1.4$, $J=2.6$, $J=17.4$, H2), 5.12 (4H, tdd, $J=1.4$, $J=2.7$, $J=10.7$, H1), 3.90-4.03 (6H, m, H8, H9, H10), 3.24 (4H, dd, $J=5.9$, $J=14.0$, H5), 3.08 (4H, dd, $J=7.2$, $J=14.0$, H4), 2.61 (4H, d, $J=6.6$, H6, H7), 1.60 (6H, s, H13) ; ^{13}C NMR 156.6 (C7), 143.4 (C10), 134.9 (C2), 127.7 (C9), 118.3 (C1), 113.9 (C8), 70.3 (C6), 66.2 (C5), 57.1 (C3), 55.9 (C4), 41.7 (C11), 31.1 (C12) ; ir/cm⁻¹ : 3424 (OH), 3079, 2972, 1643, 1614, 1513, 1454, 1191, 1084, 1040, 921, 830 ; m/z 534 (M^+), 493 ($\text{M}^+ - \text{CH}_2\text{CH}=\text{CH}_2$), 424 ($\text{M}^+ - \text{C}_7\text{H}_{12}\text{N}$), 381 ($\text{M}^+ - \text{C}_9\text{H}_{15}\text{NO}$), 228 ($\text{M}^+ - 2\text{C}_9\text{H}_{15}\text{NO}$), 213 ($\text{M}^+ - \text{CH}_3 - 2\text{C}_9\text{H}_{15}\text{NO}$), 154 ($\text{C}_9\text{H}_{16}\text{NO}^+$), 41 ($\text{CH}_2 = \text{CHCH}_2^+$).

Analysis calc. for C₃₃H₄₆N₂O₄ : C 74.12; H 8.67; N 5.24; found : C 74.11; H 8.62; N 5.14.

Preparation of N,N,N',N'-tetrakis-(3-allyloxy-2-hydroxy-1-propoxy)ethylenediamine (13)

A mixture of ethylenediamine (12) (0.057 g, 0.94 mmol) and allyl glycidyl ether (2) (0.429 g, 3.76 mmol) was heated and stirred at 80°C for 15 hours to give a product which contained mainly (13) as a yellow liquid ; ¹H NMR 5.88 (4H, tdd, J=5.6, J=11.4, J=17.3, H3), 5.28 (4H, tdd, J=1.5, J=2.3, J=17.5, H2), 5.13 (4H, tdd, J=1.5, J=2.3, J=11.3, H1), 3.75-3.99 (12H, m, H4, H5, H8), 3:37-3.39 (8H, m, H6, H7), 2.05-3.02 (12H, m, H9, H10, H11, H12) ; ir/cm⁻¹ : 3403 (OH), 2906, 1454, 1109, 1003, 937, 870

Synthesis of Carbamate Derivative (15)

A mixture of (3) (0.101 g, 0.22 mmol) and phenyl isocyanate (14) (0.063 g, 0.53 mmol) was heated and stirred at 80°C for 4 hours, then taken up in methylene chloride and washed with water. The organic layer was dried (MgSO₄) and concentrated under reduced pressure. The residue was chromatographed on a silica gel column using 5% ethyl acetate/hexane as eluent to give (15) (0.058g, 40% based on (3)) as a yellow liquid ; ¹H NMR ; 7.03-7.46 (12H, m, Ar), 6.67-6.85 (6H, m, Ar), 5.89 (2H, m, H3), 5.14-5.33 (6H, m, H1, H2, H14), 4.03-4.28 (2H, m, H8), 3.95-4.02 (8H, m, H4, H5, H9, H10), 3.51-3.76 (4H, m, H6, H7), 1.63 (8H, s, H13) ; ¹³C NMR 156.4 (C7), 152.7 (C13), 143.5 (C10), 137.7 (C14), 134.4 (C2), 129.1 (C16), 127.8 (C9), 123.6 (C17), 118.7 (C15), 117.5 (C1), 114.0 (C8), 72.4 (C4), 70.9 (C6), 69.1 (C5), 68.9 (C3), 41.7 (C11), 31.0 (C12) ; ir/cm⁻¹ 3295 (NH), 2918, 1729 (C=O), 1600, 1540, 1503, 1443, 1088, 927, 830

Synthesis of Carbamate Derivative (16)

A mixture of (9) (0.048 g, 0.12 mmol) and phenyl isocyanate (14) (0.036 g, 0.30 mmol) was heated and stirred at 80°C for 6 hours, then taken up in methylene

chloride and washed with water. The organic layer was dried (MgSO_4) and concentrated under reduced pressure. The residue was chromatographed on a silica gel column using 5% ethyl acetate/hexane as eluent to give (**16**) (0.057 g, 74% based on (**9**)) as a yellow liquid. ^1H NMR 7.62 (2H, d, $J=8.7$, H12), 7.18-7.42 (8H, m, H15, H16), 6.83-7.08 (4H, m, H11, H13), 6.75-6.82 (2H, m, H17), 5.90 (2H, m, H3), 5.14-5.47 (6H, m, H1, H2, H14), 3.98-4.50 (10H, m, H4, H5, H8, H9, H10), 3.82 (4H, m, H6, H7) ; ^{13}C NMR 157.1 (C7), 152.7 (C13), 137.6 (C14), 135.7 (C9), 134.3 (C2), 129.3 (C16), 129.0 (C11), 124.6 (C17), 123.6 (C10), 118.7 (C15), 117.6 (C1), 116.4 (C8), 106.5 (C12), 72.5 (C4), 71.9 (C6), 68.5 (C3), 68.4 (C5) ; ir/cm⁻¹ 3332 (NH), 2929, 1723 (C=O), 1637, 1605, 1543, 1443, 1083, 934, 835

Synthesis of Carbamate Derivative (**17**)

A mixture of (**11**) (0.313 g, 0.58 mmol) and phenyl isocyanate (**14**) (0.140 g, 1.18 mmol) was heated and stirred at 80°C for 24 hours, then taken up in methylene chloride and washed with water. The organic layer was dried (MgSO_4) and concentrated under reduced pressure. The residue was chromatographed on a silica gel column using 15% ethyl acetate/hexane as eluent to give (**17**) (0.152 g, 34% based on (**11**)) as a colorless liquid. ^1H NMR 7.20-7.63 (6H, m, Ar), 6.98-7.21 (6H, m, Ar), 6.65-6.92 (6H, m, Ar), 5.73-5.98 (4H, m, H3), 5.03-5.33 (10H, m, H1, H2, H14), 3.85-4.34 (6H, m, H8, H9, H10), 3.02-3.42 (8H, m, H4, H5), 2.52-2.97 (4H, m, H6, H7), 1.64 (6H, s, H13) ; ^{13}C NMR 156.5 (C7), 152.9 (C13), 143.5 (C10), 137.8 (C14), 134.9 (C2), 129.0 (C16), 127.7 (C9), 123.4 (C17), 118.7 (C15), 118.2 (C1), 113.8 (C8), 70.3 (C6), 66.2 (C5), 57.1 (C3), 55.8 (C4), 41.7 (C11), 31.0 (C12) ; ir/cm⁻¹ 3316 (NH), 2961, 1739 (C=O), 1600, 1546, 1513, 1449, 1088, 916, 835

Synthesis of Carbamate Derivative (**18**)

A mixture of (**13**) (0.308 g, 0.60 mmol) and phenyl isocyanate (**14**) (0.285 g, 2.39 mmol) was heated and stirred at 80°C for 48 hours, then taken up in methylene chloride and washed with water. The organic layer was dried (MgSO_4) and concentrated under reduced pressure. The residue was chromatographed on a silica gel

column using 15% ethyl acetate/hexane as eluent to give (**18**) (0.106 g, 20% based on (**13**)) as a colorless liquid. ^1H NMR 6.95-7.65 (20H, m, Ar), 5.86 (4H, m, H3), 5.03-5.28 (12H, m, H1, H2, H14), 3.84-4.13 (12H, m, H4, H5, H8), 3.36-3.64 (8H, m, H6, H7), 2.55-3.03 (12H, m, H9, H10, H11, H12) ; ^{13}C NMR 153.4 (C8), 138.1 (C9), 134.6 (C2), 128.9 (C11), 123.2 (C12), 118.7 (C10), 117.5 (C1), 72.3 (C4), 69.6 (C7), 67.9 (C6), 58.6 (C3), 55.8 (C5) ; ir/cm⁻¹ 3338 (NH), 2972, 1713 (C=O), 1605, 1535, 1503, 1443, 1072, 927, 835

Synthesis of polyurethane (**20**)

A mixture of (**3**) (0.154 g, 0.34 mmol) and MDI (**19**) (0.084 g, 0.34 mmol) was stirred for 10 minutes, then was heated at 120°C for 18 hours to give (**20**) (0.238 g) as a yellow solid ; ir/cm⁻¹ 3402 (NH), 2961, 1734 (C=O), 1605, 1513, 1417, 1217, 1045, 927, 830

Synthesis of polyurethane (**21**)

A mixture of (**9**) (0.024 g, 0.06 mmol) and MDI (**19**) (0.015 g, 0.06 mmol) was stirred for 10 minutes, then was heated at 120°C for 15 hours to give (**21**) (0.039 g) as a yellow solid. ir/cm⁻¹ 3400 (NH), 3067, 2914, 1720 (C=O), 1623, 1520, 1454, 1413, 1208, 1044, 921, 834

Synthesis of polyurethane (**22**)

A mixture of (**11**) (0.074 g, 0.14 mmol) and MDI (**19**) (0.035 g, 0.14 mmol) was stirred for 30 minutes to give (**21**) (0.109 g) as a yellow solid ; ir/cm⁻¹ 3360 (NH), 3074, 2966, 1713 (C=O), 1605, 1513, 1480, 1422, 1234, 1040, 916, 830

Synthesis of polyurethane (**23**)

A mixture of (**13**) (0.091 g, 0.18 mmol) and MDI (**19**) (0.089 g, 0.36 mmol) was stirred for 5 minutes, then was heated at 120°C for 24 hours to give (**23**) (0.18 g) as a yellow solid ; ir/cm⁻¹ 3390 (NH), 2919, 1725 (C=O), 1593, 1533, 1412, 1215, 1070, 923, 811

Reaction of (3) and Benzoyl peroxide (24)

A mixture of (3) (0.151 g, 0.33 mmol) and benzoyl peroxide (24) (0.004 g, 0.02 mmol) was heated at 80°C for 24 hours under nitrogen atmosphere to give (25) (0.155 g) as a brown liquid ; ir/cm⁻¹ 3424, 2972, 1745 (C=O), 1605, 1508, 1465, 1422, 1298, 1040, 916, 830

Reaction of (9) and Benzoyl peroxide (24)

A mixture of (9) (0.070 g, 0.18 mmol) and benzoyl peroxide (24) (0.004 g, 0.01 mmol) was heated at 80°C for 24 hours under nitrogen atmosphere to give (26) (0.074 g) as a brown liquid ; ir/cm⁻¹ 3418, 2939, 1723 (C=O), 1632, 1573, 1465, 1438, 1207, 1040, 927, 841

Reaction of (11) and Benzoyl peroxide (24)

A mixture of (11) (0.136 g, 0.25 mmol) and benzoyl peroxide (24) (0.004 g, 0.02 mmol) was heated and stirred at 80°C under nitrogen atmosphere for 24 hours to give (27) (0.140 g) as a yellow liquid ; ir/cm⁻¹ 3381, 2972, 1739 (C=O), 1637, 1616, 1578, 1543, 1454, 1255, 1034, 927, 835

Reaction of (13) and Benzoyl peroxide (24)

A mixture of (13) (0.121 g, 0.23 mmol) and benzoyl peroxide (24) (0.003 g, 0.01 mmol) was heated and stirred at 80°C under nitrogen atmosphere for 24 hours to give (28) (0.124 g) as a yellow liquid ; ir/cm⁻¹ 3375, 2864, 1739 (C=O), 1648, 1603, 1454, 1422, 1260, 1003, 927, 862

Reaction of polyurethane (29)

A mixture of (3) (0.093 g, 0.20 mmol), benzoyl peroxide (24) (0.002 g, 0.01 mmol), and MDI (19) (0.051 g, 0.20 mmol) was heat at 120°C for 24 hours under nitrogen atmosphere to give (29) (0.146 g) as a brown solid ; ir/cm⁻¹ 3338 (NH), 2966, 1739 (C=O), 1610, 1519, 1460, 1422, 1217, 1040, 938, 835

Reaction of polyurethane (30)

A mixture of (9) (0.075 g, 0.19 mmol), benzoyl peroxide (24) (0.002 g, 0.01 mmol), and MDI (19) (0.048 g, 0.19 mmol) was heat at 120°C for 24 hours under nitrogen atmosphere to give (30) (0.125 g) as a brown solid ; ir/cm⁻¹ 3338 (NH), 2939, 1718 (C=O), 1637, 1600, 1508, 1454, 1201, 932, 825

Reaction of polyurethane (31)

A mixture of (11) (0.089 g, 0.17 mmol), benzoyl peroxide (24) (0.002 g, 0.01 mmol), and MDI (19) (0.042 g, 0.17 mmol) was heat at 120°C for 24 hours under nitrogen atmosphere to give (31) (0.133 g) as a yellow solid ; ir/cm⁻¹ 3391 (NH), 2972, 1718 (C=O), 1664, 1610, 1503, 1411, 1239, 921, 825

Reaction of polyurethane (32)

A mixture of (13) (0.121 g, 0.23 mmol), benzoyl peroxide (24) (0.003 g, 0.01 mmol), and MDI (19) (0.116 g, 0.46 mmol) was heat at 120°C for 24 hours under nitrogen atmosphere to give (32) (0.240 g) as a yellow solid ; ir/cm⁻¹ 3375 (NH), 2918, 1713 (C=O), 1600, 1524, 1417, 1217, 921, 819