

Supplementary Information Part 1
for

An Experimental and Computational Investigation of the Diels-Alder Cycloadditions of Halogen Substituted 2(H)-Pyran-2-ones

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General Experimental

Nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ using instruments operating at 360, 400 and 500 MHz for ¹H and corresponding values for ¹³C. All chemical shifts () are reported in parts per million (ppm) and are referenced internally with tetramethylsilane at 0 ppm. ¹³C NMR spectra are assigned with the help of DEPT analysis, proton spectra are assigned with the help of COSY and NOSEY experiments where necessary. Multiplicity of the signal is reported as singlet (s), doublet (d), double doublet (dd), double double doublet (ddd), double triplet (dt), double multiplet (dm), triplet (t), multiplet (m), quartet (q) and quintet (quintet).

Sodium chloride plates were used to run the Infra red spectra. Solids were run as a dispersion in nujol, unless otherwise stated, and oils were run neat. Unloaded plates were run blank as background.

All melting points are uncorrected.

Techniques used for mass spectrometry were electron impact (EI), chemical ionisation (CI) or fast atom bombardment (FAB). Technique used for determination of exact mass was electrospray (ESI). 3-Bromo-2(H)-pyran-2-one,¹ 5-bromo-2(H)pyran-2-one,¹ 4-chloro-2(H)-pyran-2-one,² 3-(trimethylstannyl)-2(H)-pyran-2-one,³ and 5-(trimethylstannyl)-2(H)-pyran-2-one³ were prepared according to literature procedure.

3-(Tributylstannyl)-2(H)-pyran-2-one, 7.

In a dry round-bottom flask, hexa(n-butyl)ditin (8.5 g, 7.4 mL, 14.64 mmol), 3-bromo-2(H)-pyran-2-one **4** (2.11 g, 12.0 mmol) and Pd(PPh₃)₄ (423 mg, 0.363 mmol) were added to tetrahydrofuran (20 mL). The mixture was refluxed under an argon atmosphere for 43 h, then cooled to room temperature. The solvent was removed under reduced pressure and the crude material was purified by flash chromatography, eluting with 20% v/v ether in petrol ether (60-80 °C) to give 3.48 g (76%) of a yellow oil. ¹H NMR 7.43 (dd, 1 H, J = 2.2 Hz, 5.1 Hz, H-6), 7.37 (dd, 1H, J = 2.2 Hz, 6.0 Hz, H-4), 6.13 (dd, 1H, J = 5.2 Hz, 6.0 Hz, H-5), 1.52 (m, 6H, 3 x SnCH₂Pr), 1.33 (m, 6H, CH₂Et), 1.08 (m, 6H, 3 x CH₂Me), 0.89 (t, 9H, J = 7.3 Hz, 3 x CH₃); ¹³C NMR 165.3 (C-2), 152.0 (C-6), 151.5 (C-4), 133.4 (C-3), 107.1 (C-5), 29.3 (3 x SnCH₂), 27.7 (3 x SnCH₂CH₂), 14.0 (3 x CH₃), 10.1 (J_{Sn} = 356.8 Hz, 340.9 Hz, 3 x SnCH₂); IR 3092, 2957, 2925, 2871, 2853, 1706, 1621, 1526, 1464, 1376, 1331, 1237, 1129, 1083, 958, 875, 779, 693, 670, 600 cm⁻¹; m/z 329 [100, (M⁺-nBu)], 328 (36), 327 (75), 326 (29), 325 (43), 315 (54), 313 (81), 311 (55), 259 (13), 257 (20), 255 (14), 215 [25, (MH⁺ - 3 x nBu)], 213 (21), 201 (12), 199(17), 197 (12), 177 (18), 175 (13), 121 (9), 117 (5), 57 (15); HRMS calcd for C₁₃H₂₁O₂Sn (M⁺-nBu): 329.05634, found: 329.05718.

5-(Tributylstannyl)-2(H)-pyran-2-one, 8b.

In a dry round-bottom flask, hexa(n-butyl)ditin (0.80 mL, 1.58 mmol), 5-bromo-2(H)-pyran-2-one **5** (199 mg, 1.14 mmol) and Pd(PPh₃)₄ (41 mg, 35 μmol) were added to toluene (5 mL). The mixture was refluxed under an argon atmosphere for 69 h, then cooled to room temperature. The solvent was removed under reduced pressure and the crude material was purified by flash chromatography, eluting with 20% v/v ethyl acetate in petrol ether (60-80 °C) to give 163 mg (37%) of a yellow oil. ¹H NMR

7.25 (dd, 1 H, $J = 2.0$ Hz, 9.1 Hz, H-4), 7.19 (dd, 1H, $J = 1.3$ Hz, 2.0 Hz, H-6), 6.33 (dd, 1H, $J = 1.3$ Hz, 9.1 Hz, H-3), 1.21-1.75 (m, 18H, 9 x CH₂), 0.92 (t, 9H, $J = 7.5$ Hz, 3 x CH₃); ¹³C NMR 162.6 (C-2), 154.7 (C-4), 149.2 (C-6), 117.6 (C-3), 113.1 (C-5), 29.3 (3 x CH₂), 27.6 (3 x CH₂), 14.0 (3 x CH₃), 10.1 ($J_{\text{Sn}} = 354.1$ Hz, 338.4 Hz, CH₂); IR 2958, 2913, 2857, 1740, 1712, 1606, 1580, 1521, 1460, 1410, 1373, 1337, 1217, 1129, 1071, 1021, 959, 873, 826 cm⁻¹; m/z 387 (2, M⁺), 385 (2, M⁺), 329 [37, (MH⁺-nBu)], 328 (14), 327 (29), 326 (12), 325 (17), 319 (11), 317 (19), 315 (65), 314 (25), 313 (100), 312 (35), 311 (69), 310 (17), 309 (27), 295 (10), 291 (56), 290 (20), 289 (42), 288 (17), 287 (24), 259 (17), 257 (27), 255 (20), 215 [6, (MH⁺ - 3 x nBu)], 177 (15), 175 (11); HRMS calcd for C₁₇H₃₀O₂Sn: 409.11720, found: 409.11610.

4-(Trimethylstannyl)-2(H)-pyran-2-one, **9**.

In a dry round-bottom flask, hexamethylditin (1.19 g, 3.63 mmol), 4-chloro-2(H)-pyran-2-one **6** (0.39 g, 3.0 mmol) and Pd(PPh₃)₄ (0.12 g, 0.09 mmol) were added to tetrahydrofuran (6 mL). The mixture was refluxed under an argon atmosphere for 44 h, then cooled to room temperature. The solvent was removed under reduced pressure and the crude material was purified by silica gel chromatography, eluting with 30% v/v ether in petrol ether (60-80 °C) to give 490 mg (63%) of a white solid. m.p. 40 °C; ¹H NMR 7.39 (dd, 1H, $J = 1.3$ Hz, 5.0 Hz, H-5), 6.46 (dd, 1H, $J = 0.9$ Hz, 1.3Hz, H-3), 6.24 (dd, 1H, $J = 0.9$ Hz, 5.0 Hz, H-6), 0.33 [s, 9H, $J_{\text{Sn}} = 27.3$ Hz, 28.3 Hz, Sn(CH₃)₃]; ¹³C NMR 164.3 (C-2), 160.1 (C-4), 149.3 (C-5), 125.0 (C-3), 111.8 (C-6), -9.4 [$J_{\text{Sn}} = 408$ Hz, Sn(CH₃)₃]; IR 3064, 2915, 1700, 1645, 1598, 1251, 1192, 1175, 1096, 999, 862, 807, 782, 573, 531 cm⁻¹; m/z 260 (39, M⁺), 258 (29), 256 (19), 245 (82, M⁺ - Me), 244 (26), 243 (61), 242 (24), 241 (39), 232 (95, M⁺ - 2 x Me), 231 (31), 230 (69, M⁺ - 2 x Me), 229(29), 228 (42), 217 (74, M⁺ - 3 x Me), 216 (27), 215 (57, M⁺ - 3 x Me), 214 (22), 213 (38), 187 (22), 185 (20), 183 (14), 169 (20), 167 (18), 165 (100, ¹²⁰SnMe₃), 164 (31,

$^{119}\text{SnMe}_3$), 163 (78, $^{118}\text{SnMe}_3$), 162 (28, $^{117}\text{SnMe}_3$), 161 (55, $^{116}\text{SnMe}_3$), 150 (37), 149 (23), 148 (34), 135 (41), 133 (32), 131 (21), 120 (18), 119(12), 118 (14), 95 (16, $\text{M}^+ - \text{SnMe}_3$), 81 (6), 69 (9); HRMS calcd for $\text{C}_8\text{H}_{12}\text{O}_2\text{SnNa}$: 282.97570; found: 282.97523.

3-Chloro-2(H)-pyran-2-one, 10.

To a solution of 3-(tributylstannyl)-2(H)-pyran-2-one **7** (1.0 g, 2.6 mmol) in dry dichloromethane (50 mL, 0.05 mmol/mL) was added a solution of chlorine gas (227 mg, 3.2 mmol, 1.2 equiv.) in carbon tetrachloride (43 mL, 0.075 mmol/mL) during 10 min *via* syringe. The resulting solution was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, eluting with 30% v/v ethyl acetate in petrol ether (60-80 °C) to afford 316 mg (93%) of a white solid. m.p. 82 °C; $^1\text{H NMR}$ 7.48 (dd, 1 H, $J = 1.9$ Hz, 7.0 Hz, H-6), 7.47 (dd, 1H, $J = 1.9$ Hz, 5.2 Hz, H-4), 6.23 (dd, 1H, $J = 5.2$ Hz, 7.0 Hz, H-5); $^{13}\text{C NMR}$ 158.9 (C-2), 150.6 (C-6), 140.3 (C-4), 123.8 (C-3), 106.1 (C-5); IR 3104, 3066, 3028, 1722, 1627, 1528, 1335, 1226, 1094, 1014, 986, 962, 863, 778, 745 cm^{-1} ; m/z 132 (33, M^+ for ^{37}Cl), 130 (100, M^+ for ^{35}Cl), 104 (18), 102 (56), 74 (9), 73 (8), 39 (17); HRMS calcd for $\text{C}_{10}\text{H}_6\text{Cl}_2\text{O}_4\text{Na}$ [(2M+Na) $^+$]: 282.95356; found: 282.95360.

3-Iodo-2(H)-pyran-2-one, 11.

A solution of 3-(tributylstannyl)-2(H)-pyran-2-one **7** (793 mg, 2.06 mmol) in chloroform (40 mL) was placed in a dry round-bottom flask wrapped with aluminum foil. Then a solution of iodine (523 mg, 2.06 mmol) in chloroform (100 mL) was added, *via* pressure equalising addition funnel, during 20 min. The resulting mixture was stirred at room temperature for 6 days. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, eluting with 30% v/v ether in petrol ether (60-80 °C) to give 380 mg (83%) of a yellowish solid. m.p. 66 °C; $^1\text{H NMR}$ 7.95 (dd, 1

H, J = 1.9 Hz, 6.8 Hz, H-6), 6.52 (dd, 1H, J = 1.9 Hz, 5.0 Hz, H-4), 6.01 (dd, 1H, J = 5.0 Hz, 6.8 Hz, H-5). ^{13}C NMR 158.6 (C-2), 152.0 (C-6), 151.6 (C-4), 107.3 (C-5), 86.8 (C-3); IR 3098, 2967, 2923, 2852, 1713, 1622, 1522, 1464, 1378, 1329, 1235, 1091, 959, 837, 752, 640 cm^{-1} ; m/z 222 (100, M^+), 194 (28), 165 (5), 95 [8, ($\text{M}^+ - \text{I}$)]; HRMS calcd for $\text{C}_5\text{H}_3\text{IO}_2\text{Na}$: 244.90699, found: 244.90705.

5-Chloro-2(H)-pyran-2-one, 12.

Method A: To a solution of 5-(tiburystannyl)-2(H)-pyran-2-one **8b** (585 mg, 1.52 mmol) in dry dichloromethane (30 mL, 0.05 mmol/mL) was added *via* syringe to a solution of chlorine gas (142 mg, 2 mmol, 1.3 equiv.) in carbon tetrachloride (27 mL, 0.075 mmol/mL) during 10 min. The resulting solution was stirred at room temperature for 18h. The solvent was removed under reduced pressure and the residue purified by flash chromatography, eluting with 20% v/v ethyl acetate in petrol ether (60-80 °C) to afford 129 mg (67%) of a white solid.

Method B:⁴ To a solution of coumalic acid (2.67 g, 19 mmol) in acetonitrile and water (5:1, 120 mL) were added N-chlorosuccinimide (5.09g, 38 mmol) and lithium acetate (2.52 g, 38 mmol) respectively. The resulting mixture was stirred at room temperature for 6 days after which it was diluted with water (100 mL) and was extracted with ethyl acetate (4 x 100 mL). The combined organic layers were dried over magnesium sulphate and the solvent removed under reduced pressure. The residue was purified by flash chromatography, eluting with 20% v/v ethyl acetate in petrol ether (60-80°C) to give 200 mg (8%) of the desired product as a yellow solid together with ca 4% of 3,5-dichloropyrone. m.p. 54-58 °C (dec.); ^1H NMR 7.59 (dd, 1 H, J = 0.9 Hz, 2.6 Hz, H-6), 7.34 (dd, 1H, J = 2.6 Hz, 9.9 Hz, H-4), 6.30 (dd, 1H, J = 0.9 Hz, 9.9 Hz, H-3); ^{13}C NMR 159.9 (C-2), 150.1 (C-6), 146.4 (C-4), 118.0 (C-3), 101.2 (C-5); IR 3076, 2925, 2855, 1749, 1621, 1536, 1227, 1170, 1127, 1071, 945, 834, 785, 730, 664

cm^{-1} ; m/z 132 (33, M^+ for ^{37}Cl), 130 (100, M^+ for ^{35}Cl), 104 (20), 102 (60), 74 (19), 73 (25); Anal. calcd for $\text{C}_5\text{H}_3\text{ClO}_2$: C, 46.01, H, 2.32; found: C, 45.91, H, 2.43.

5-Iodo-2(H)-pyran-2-one, 13.

A solution of 5-(trimethylstannyl)-2(H)-pyran-2-one **8a** (340 mg, 1.3 mmol) in chloroform (25 mL) was placed in a dry round-bottom flask wrapped with aluminum foil. Then a solution of iodine (340 mg, 1.34 mmol) in chloroform (50 mL) was added, *via* pressure equalising addition funnel, during 20 min. The resulting mixture was stirred at room temperature for 6 days. The solvent was removed under reduced pressure and the residue was purified by flash chromatography, eluting with 20% v/v ethyl acetate in petrol ether (60-80 °C) to give 160 mg (56%) of a yellowish solid. m.p. 100 °C; ^1H NMR 7.62 (dd, 1H, $J = 1.0$ Hz, 2.5 Hz, H-6), 7.38 (dd, 1H, $J = 2.5$ Hz, 9.7 Hz, H-4), 6.22 (dd, 1H, $J = 1.0$ Hz, 9.7 Hz, H-3); ^{13}C NMR 159.3 (C-2), 153.9 (C-6), 149.7 (C-4), 118.3 (C-3), 67.6 (C-5); IR 3056, 2978, 2923, 2852, 1734, 1711, 1594, 1523, 1464, 1378, 1323, 1215, 1147, 1122, 1025, 941, 857, 829, 791, 625, 602 cm^{-1} ; m/z 222 (100, M^+), 194 (54), 166 (9), 127 (5, I^+), 95 [16, ($M^+ - \text{I}$)], 67 (5), 39 (34); HRMS calcd for $\text{C}_5\text{H}_3\text{IO}_2\text{Na}$: 244.90699; found: 244.90685.

4-Bromo-2(H)-pyran-2-one, 14.

A solution of 4-(trimethylstannyl)-2(H)-pyran-2-one **9** (260 mg, 1 mmol) in chloroform (20 mL) was cooled to -60 °C and one equivalent of a solution of bromine (160 mg, 2 mmol) in chloroform (40 mL) was added *via* a syringe over 15 minutes. After addition the cold bath was removed and the reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue purified by silica gel chromatography, eluting with 30% v/v ethyl acetate in petrol ether (60-80 °C) to give 169 mg (96%) of a yellow solid. m.p. 49 °C; ^1H NMR 7.37 (dd, 1 H, $J = 0.8$ Hz, 5.6

Hz, H-6), 6.65 (dd, 1H, J = 0.8 Hz, 1.8 Hz, H-3), 6.40 (dd, 1H, J = 1.8 Hz, 5.6 Hz, H-5); ^{13}C NMR 159.7 (C-2), 150.7 (C-6), 140.0 (C-4), 118.6 (C-3), 111.1 (C-5); IR 3031, 1730, 1648, 1609, 1535, 1406, 1293, 1237, 1167, 1083, 1013, 968, 957, 864, 811, 783, 722, 661, 612, 575 cm^{-1} ; m/z 176 (68, M^+ for ^{81}Br), 174 (69, M^+ for ^{79}Br), 147 [99, ($\text{M}^+ - 29$)], 145 [100, ($\text{M}^+ - 29$)], 132 (5), 130 (9), 119 (18), 117 (17), 95 [13, ($\text{M}^+ - \text{Br}$)], 80 (5, Br^+), 67 (48), 50 (12), and 39 (86), 38 (38), 37 (22); HRMS calcd for $\text{C}_5\text{H}_3^{81}\text{BrO}_2$: 175.92905, found: 175.92919.

4-Iodo-2(H)-pyran-2-one, 15.

A solution of 4-(trimethylstannyl)-2(H)-pyran-2-one **9** (610 mg, 2.35 mmol) in chloroform (40 mL) was placed in a dry round-bottom flask wrapped with aluminum foil. Then a solution of iodine (600 mg, 2.36 mmol) in chloroform (80 mL) was added, *via* pressure equalising addition funnel, during 20 min. The resulting mixture was stirred at room temperature for 6 days. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography, eluting with 35% v/v ether in petrol ether (60-80 °C) to give 320 mg (61%) of a yellow solid. m.p. 50 °C; ^1H NMR 7.21 (dd, 1 H, J = 0.9 Hz, 5.5 Hz, H-6), 6.95 (dd, 1H, J = 0.9 Hz, 1.6 Hz, H-3), 6.53 (dd, 1H, J = 1.6 Hz, 5.5 Hz, H-5); ^{13}C NMR 158.9 (C-2), 149.9 (C-6), 125.9 (C-3), 115.5 (C-5), 113.7 (C-4); IR 2923, 2852, 1724, 1646, 1601, 1563, 1519, 1403, 1288, 1241, 1169, 1088, 1004, 960, 846, 813, 795, 721, 651, 599, 574 cm^{-1} ; m/z 222 (96, M^+), 194 (100, $\text{M}^+ - 28$); HRMS calcd for $\text{C}_5\text{H}_3\text{IO}_2\text{Na}$: 244.90699; found: 244.90802.

Cycloaddition of 4-Bromo-2(H)-pyran-2-one and Methyl Acrylate

A sealed pressure tube (purchased from Aldrich Chemical Co Cat No Z18, 109-9) was charged with 4-bromo-2(H)-pyran-2-one **14** (88 mg, 0.5 mmol), methyl acrylate (0.3 mL, 3.33 mmol, 5 equiv), a few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic

stirrer bar. The pressure tube was sealed and immersed in an oil bath maintained at 50 °C. After 14 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of four isomers of cycloadducts and unreacted starting material (ca 9%). Chromatography using 20% v/v ethyl acetate in petrol ether afforded pure samples of the 6-*endo*, 5-*endo* and 5-*exo* cycloadducts and a sample of the 6-*exo* cycloadduct contaminated with small quantity of 5-*endo* cycloadduct. Combined isolated yield of cycloadducts was 102 mg, 78%.

Methyl 8-bromo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-6-*endo*-carboxylate ^1H NMR 6.62 (dd, 1H, $J_{4,7} = 2.2$ Hz, $J_{1,7} = 5.4$ Hz, H-7), 5.45 (dd, 1H, $J_{1,6} = 3.6$ Hz, $J_{1,7} = 5.4$ Hz, H-1), 3.73 (s, 3H, CO_2CH_3), 3.70 (m, 1H, H-4), 3.33 (ddd, 1H, $J_{1,6} = 3.6$ Hz, $J_{5\text{endo},6} = 5.7$ Hz, $J_{5\text{exo},6} = 9.5$ z, H-6), 2.28 (ddd, 1H, $J_{4,5\text{exo}} = 3.2$ Hz, $J_{5\text{exo},6} = 9.5$ z, $J_{5\text{exo},5\text{endo}} = 13.3$ z, H-5_{exo}), 2.16 (ddd, 1H, $J_{4,5\text{endo}} = 2.5$ Hz, $J_{5\text{endo},6} = 5.7$ z, $J_{5\text{endo},5\text{exo}} = 13.3$ z, H-5_{endo}); ^{13}C NMR 171.1 ($\underline{\text{C}}\text{O}_2\text{Me}$), 171.0 (C-3), 130.2 (C-7), 124.0 (C-8), 75.2 (C-1), 53.1 ($\text{CO}_2\underline{\text{C}}\text{H}_3$), 50.6 (C-4), 43.6 (C-6), 24.8 (C-5); IR 3090, 3007, 2955, 2923, 2852, 1764, 1737, 1614, 1436, 1354, 1324, 1300, 1201, 1137, 1088, 1032, 1012, 993, 973, 955, 894, 845, 830, 806, 764, 735, 695, 573, 523 cm^{-1} ; m/z 263 (21, MH^+ for ^{81}Br), 262 (13, M^+ for ^{81}Br), 261 (21, MH^+ for ^{79}Br), 260 (12, M^+ for ^{79}Br), 245 (100), 243 (100), 231 [79, (M^+ -OMe)], 229 [80, (M^+ -OMe)], 218 [36, (M^+ - CO_2)], 216 [37, (M^+ - CO_2)], 187 [8, (M^+ - CO_2Me)], 185 (16, 229 - CO_2), 159 (50), 158 (40), 157 (52), 156 (38), 147 (21), 145 (22), 137 [42, (M^+ - $\text{CO}_2\text{-Br}$)], 93 (19), 78 (47), 77 (50), 59 (11), 51 (18); HRMS calcd for $\text{C}_9\text{H}_9^{81}\text{BrO}_4\text{Na}$: 284.95559; found: 284.95594.

Methyl 8-bromo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5-*endo*-carboxylate ^1H NMR 6.71 (dd, 1H, $J_{4,7} = 2.1$ Hz, $J_{1,7} = 5.6$ Hz, H-7), 5.26 (dd, 1H, $J_{1,6\text{endo}} = 1.5$ Hz, $J_{1,6\text{exo}} = 3.7$ Hz, $J_{1,7} = 5.6$ Hz, H-1), 4.09 (m, 1H, H-4), 3.76 (s, 3H, CO_2CH_3), 3.15 (dt, 1H, $J_{4,5} = 3.3$ Hz, $J_{5,6\text{endo}} = 3.3$ Hz, $J_{5,6\text{exo}} = 9.4$ Hz, H-

5), 2.43 (ddd, 1H, $J_{1,6\text{exo}} = 3.7$ Hz, $J_{5,6\text{exo}} = 9.4$ Hz, $J_{6\text{exo},6\text{endo}} = 13.8$ Hz, H-6_{exo}), 2.23 (ddd, 1H, $J_{1,6\text{endo}} = 1.5$ Hz, $J_{5,6\text{endo}} = 3.3$ Hz, $J_{6\text{endo},6\text{exo}} = 13.8$ Hz, H-6_{endo}); ^{13}C NMR 170.8 (CO₂CH₃), 170.0 (C-3), 132.5 (C-7), 120.0 (C-8), 74.8 (C-1), 52.7 (CO₂CH₃), 52.4 (C-4), 36.9 (C-5), 29.3 (C-6); IR 3005, 2954, 2924, 2852, 1761, 1737, 1615, 1436, 1356, 1324, 1271, 1231, 1210, 1173, 1073, 1042, 992, 949, 904, 891, 846, 788, 765, 693, 633, 509 cm⁻¹; m/z 263 (4, MH⁺ for ⁸¹Br), 262 (5, M⁺ for ⁸¹Br), 261 (4, MH⁺ for ⁷⁹Br), 260 (4, M⁺ for ⁷⁹Br), 245 (32), 243 (32), 219 [10, (MH⁺-CO₂)], 218 [26, (M⁺-CO₂)], 217 (17), 216 [26, (M⁺-CO₂)], 215 (13), 187 (7), 185 (4), 173 (10), 159 [95, (M⁺-CO₂-CO₂Me)], 158 (30), 157 [100, (M⁺-CO₂-CO₂Me)], 156 (24), 147 (10), 145 (11), 137 (36), 93 (18), 78 (53), 77 (63), 59 (9), 51 (20), 50 (10); HRMS calcd for C₉H₉⁸¹BrO₄Na: 284.95559; found: 284.95627.

Methyl 8-bromo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-6_{exo}-carboxylate ^1H NMR 6.67 (dd, 1H, $J_{4,7} = 2.1$ Hz, $J_{1,7} = 5.6$ Hz, H-7), 5.51 (dd, 1H, $J_{1,6} = 1.5$ Hz, $J_{1,7} = 5.6$ Hz, H-1), 3.78 (s, 3H, CO₂CH₃), 3.70 (m, 1H, H-4), 2.86 (ddd, 1H, $J_{1,6} = 1.5$ Hz, $J_{5\text{exo},6} = 3.3$ Hz, $J_{5\text{endo},6} = 10.7$ Hz, H-6), 2.55 (dt, 1H, $J_{4,5\text{exo}} = 2.7$ Hz, $J_{5\text{exo},6} = 3.3$ Hz, $J_{5\text{exo},5\text{endo}} = 13.5$ Hz, H-5_{exo}), 2.03 (ddd, 1H, $J_{4,5\text{endo}} = 2.7$ Hz, $J_{5\text{endo},6} = 10.8$ Hz, $J_{5\text{endo},5\text{exo}} = 13.5$ Hz, H-5_{endo}); ^{13}C NMR 170.8 (CO₂CH₃), 170.0 (C-3), 130.7 (C-7), 120.0 (C-8), 76.3 (C-1), 52.9 (CO₂CH₃), 50.3 (C-4), 43.3 (C-6), 23.0 (C-5).

Methyl 8-bromo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5_{exo}-carboxylate ^1H NMR 6.70 (dd, 1H, $J_{4,7} = 2.1$ Hz, $J_{1,7} = 5.5$ Hz, H-7), 5.25 (ddd, 1H, $J_{1,6\text{endo}} = 1.7$ Hz, $J_{1,6\text{exo}} = 3.6$ Hz, $J_{1,7} = 5.5$ Hz, H-1), 3.91 (t, 1H, $J = 2.1$ Hz, H-4), 3.77 (s, 3H, CO₂CH₃), 2.93 (ddd, 1H, $J_{4,5} = 2.2$ Hz, $J_{5,6\text{exo}} = 5.6$ Hz, $J_{5,6\text{endo}} = 10.7$ Hz, H-5), 2.51 (ddd, 1H, $J_{1,6\text{exo}} = 3.6$ Hz, $J_{5,6\text{exo}} = 5.6$ Hz, $J_{6\text{exo},6\text{endo}} = 13.9$ Hz, H-6_{exo}), 2.05 (ddd, 1H, $J_{1,6\text{endo}} = 1.7$ Hz, $J_{5,6\text{endo}} = 10.7$ Hz, $J_{6\text{exo},6\text{endo}} = 13.9$ Hz, H-6_{endo}); ^{13}C NMR 172.1 (CO₂CH₃), 169.4 (C-3), 135.3 (C-8), 128.4 (C-7), 74.2 (C-1), 53.3 (CO₂CH₃), 51.7 (C-4), 39.2 (C-5), 30.5 (C-6); IR 2923, 2852, 1765, 1738, 1658, 1464, 1355, 1264, 1207, 1134, 1032, 996, 908, 742 cm⁻¹;

m/z 263 (4, MH⁺ for ⁸¹Br), 261 (4, MH⁺ for ⁷⁹Br), 245 (4), 243 (4), 231 [6, (M⁺-OMe)], 229 [6, (M⁺-OMe)], 218 [16, (M⁺-CO₂)], 216 [17, (M⁺-CO₂)], 217 (8), 187 [5, (M⁺-CO₂Me)], 185 [5, (M⁺-CO₂Me)], 159 [99, (M⁺-CO₂-CO₂Me)], 158 (27), 157 [100, (M⁺-CO₂-CO₂Me)], 156 (19), 147 (10), 145 (12), 137 (34), 93 (21), 78 (25), 77 (41), 59 (8); HRMS calcd for C₉H₉⁸¹BrO₄Na: 284.95559; found: 284.95539.

Cycloaddition of 4-Iodo-2(H)-pyran-2-one and Methyl Acrylate

A sealed pressure tube (purchased from Aldrich Chemical Co Cat No Z18, 109-9) was charged with 4-iodo-2(H)-pyran-2-one **15** (52 mg, 0.23 mmol), methyl acrylate (0.5 mL, 5.6 mmol, 24 equiv), a few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and immersed in an oil bath maintained at 50 °C. After 15 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of four isomers of cycloadducts and a trace of unreacted starting material. Silica gel chromatography using 20-50% v/v ethyl acetate in petrol ether afforded a pure sample of the 5-*exo* cycloadduct and a mixture of 5-*endo* and 6-*endo* cycloadducts from which the former was isolated by crystallisation. Combined isolated yield of cycloadducts was 67 mg, 93%.

Methyl 8-iodo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-6_{endo}-carboxylate ¹H NMR 6.86 (dd, 1H, J_{4,7} = 1.8 Hz, J_{1,7} = 5.2 Hz, H-7), 5.27 (dd, 1H, J_{1,6} = 3.7 Hz, J_{1,7} = 5.1 Hz, H-1), 3.70 (m, 1H, H-4), 3.66 (s, 3H, CO₂CH₃), 3.23 (ddd, 1H, J_{1,6} = 3.7 Hz, J_{5_{endo},6} = 5.8 Hz, J_{5_{exo},6} = 9.4 Hz, H-6), 2.4 - 1.90 (m, 2H, H-5); ¹³C NMR 171.2 (C=O), 171.0 (C-3), 139.1 (C-7), 93.7 (C-8), 75.7 (C-1), 53.6 (C-4), 53.1 (CO₂CH₃), 43.6 (C-6), 24.7 (C-5).

Methyl 8-iodo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5_{endo}-carboxylate m.p. 100-101 °C; ¹H NMR 6.96 (dd, 1H, J_{4,7} = 1.8 Hz, J_{1,7} = 5.4 Hz, H-7), 5.07 (m, 1H, H-1), 4.10 (3, 1H, H-4), 3.70 (s, 3H, CO₂CH₃), 3.06 (dt, 1H, J_{4,5} = 3.3 Hz, J_{5,6endo} = 3.3 Hz, J_{5,6exo} = 9.3 Hz, H-5), 2.40 - 1.90 (m, 2H, H-6); ¹³C NMR 171.3 (CO₂CH₃), 171.0 (C-3), 141.9 (C-7), 89.2 (C-8), 75.8 (C-1), 55.0 (C-4), 53.0 (CO₂CH₃), 37.3 (C-5), 29.4 (C-6); IR 3457, 3075, 3003, 2952, 2846, 1757, 1738, 1598, 1436, 1355, 1326, 1270, 1232, 1209, 1172, 1074, 1041, 1008, 992, 949, 902, 848, 788, 765, 735, 683 cm⁻¹; m/z 309 (6), 308 (17, M⁺), 277 (6), 276 (6), 264 [22, (M⁺-CO₂)], 248 (8), 222 [9, (M⁺-86, retro Diels-Alder)], 205 [51, (M⁺-CO₂-CO₂Me)], 204 (19), 127 (5), 93 (21), 79 (8), 78 (100), 77 (17), 65 (11), 59 (10), 55 (18), 51 (10), 50 (10); HRMS calcd for C₉H₉IO₄Na: 330.94452; found: 330.94355.

Methyl 8-iodo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5_{exo}-carboxylate ¹H NMR 7.00 (dd, 1H, J_{4,7} = 1.8 Hz, J_{1,7} = 5.3 Hz, H-7), 5.13 (ddd, 1H, J_{1,6endo} = 1.7 Hz, J_{1,6exo} = 3.6 Hz, J_{1,7} = 5.3 Hz, H-1), 3.97 (t, 1H, J_{4,7} J_{4,5} = 2.0 Hz, H-4), 3.76 (s, 3H, CO₂CH₃), 2.85 (ddd, 1H, J_{4,5} = 2.2 Hz, J_{5,6exo} = 5.6 Hz, J_{5,6endo} = 10.7 Hz, H-5), 2.47 (ddd, 1H, J_{1,6exo} = 3.6 Hz, J_{5,6exo} = 5.6 Hz, J_{6exo,6endo} = 13.8 Hz, H-6_{exo}), 2.02 (ddd, 1H, J_{1,6endo} = 1.7 Hz, J_{5,6endo} = 10.7 Hz, J_{6endo,6exo} = 13.8 Hz, H-6_{endo}); ¹³C NMR 171.9 (CO₂CH₃), 169.4 (C-3), 142.1 (C-7), 91.7 (C-8), 75.2 (C-1), 56.0 (C-4), 53.3 (CO₂CH₃), 39.1 (C-5), 30.2 (C-6); IR 2956, 2924, 2853, 1760, 1734, 1599, 1463, 1355, 1261, 1206, 1175, 1095, 1028, 857, 803, 739 cm⁻¹; m/z 309 (3), 308 (7, M⁺), 264 [23, (M⁺-CO₂)], 222 [7, (M⁺-86, retro Diels-Alder)], 205 [62, (M⁺-CO₂-CO₂Me)], 148 (11), 101 (12), 93 (23), 85 (14), 83 (16), 79 (10), 78 (100), 77 (15), 73 (12), 71 (12), 69 (12), 59 (21), 57 (21), 55 (16), 51 (9), 50 (5); HRMS calcd for C₉H₉IO₄Na: 330.94452; found: 330.94473.

Cycloaddition of 4-Bromo-2(H)-pyran-2-one and Acrylonitrile

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 4-Bromo-2(H)-pyran-2-one **14** (44 mg, 0.25 mmol), acrylonitrile (0.5 mL, 7.6 mmol, 30 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 50 °C for 15 days then at 70 °C for 17 days. The tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of four cycloadducts, as a 1:1 mixture of 5- and 6-substituted isomers. Silica gel chromatography, using 20% v/v ethyl acetate in petroleum ether, afforded pure samples of the 6-*endo* and 5-*exo* cycloadducts as well as a mixed sample of 5-*endo* and 6-*exo* cycloadducts. Combined isolated yield of cycloadducts was 43 mg, 75%.

8-Bromo-6_{endo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 109-110 °C ; ¹H NMR 6.79 (dd, 1H, J_{4,7} = 2.0 Hz, J_{1,7} = 5.5 Hz, H-7), 5.39 (dd, 1H, J_{1,6} = 3.5 Hz, J_{1,7} = 5.5 Hz, H-1), 3.79 (m, 1H, H-4), 3.38 (ddd, 1H, J_{1,6} = 3.5 Hz, J_{5endo,6} = 5.3 Hz, J_{6,5exo} = 9.4 Hz, H-6), 2.49 (ddd, 1H, J_{4,5exo} = 3.0 Hz, J_{5exo,6} = 9.4 Hz, J_{5exo,5endo} = 13.4 Hz, H-5_{exo}), 2.08 (ddd, 1H, J_{4,5endo} = 2.5 Hz, J_{5endo,6} = 5.3 Hz, J_{5endo,5exo} = 13.4 Hz, H-5_{endo}); ¹³C NMR 169.0 (C-3), 129.6 (C-7), 125.3 (C-8), 118.2 (CN), 73.8 (C-1), 49.9 (C-4), 28.8 (C-6), 26.6 (C-5); IR 2923, 2853, 2248, 1769, 1614, 1463, 1359, 1208, 1141, 1067, 1013, 995, 961, 924, 838, 738, 690, 534 cm⁻¹; m/z 229 (8, M⁺ for ⁸¹Br), 228 (3, M⁺), 227 (7, M⁺ for ⁷⁹Br), 185 [28, (M⁺ for ⁸¹Br-CO₂)], 183 [28, (M⁺ for ⁷⁹Br-CO₂)], 176 [32, (M⁺ for ⁸¹Br-53, retro Diels-Alder)], 174 [32, (M⁺ for ⁷⁹Br-53, retro Diels-Alder)], 147 (36), 145 (36), 104 [100, (M⁺-CO₂-Br)], 103 (12), 102 (11), 77 (38), 67 (11), 51 (17), 50 (11); HRMS calcd for C₈H₇⁸¹BrNO₂ (MH⁺): 229.96342; found: 229.96392.

8-Bromo-5_{endo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene and **8-Bromo-6_{exo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene** ¹H NMR 5-endo cycloadduct 6.89 (dd, 1H, $J_{4,7} = 2.1$ Hz, $J_{1,7} = 5.7$ Hz, H-7), 5.33 (ddd, 1H, $J_{1,6endo} = 1.6$ Hz, $J_{1,6exo} = 3.4$ Hz, $J_{1,7} = 5.7$ Hz, H-1), 3.99 (m, 1H, H-4), 3.29 (dt, 1H, $J_{4,5} = 3.1$ Hz, $J_{5,6endo} = 3.1$ Hz, $J_{5,6exo} = 9.5$ Hz, H-5), 2.66 (ddd, 1H, $J_{1,6exo} = 3.4$ Hz, $J_{5,6exo} = 9.5$ Hz, $J_{6exo,6endo} = 14.0$ Hz, H-6_{exo}), 2.06 (ddd, 1H, $J_{1,6endo} = 1.6$ Hz, $J_{5,6endo} = 3.3$ Hz, $J_{6exo,6endo} = 14.0$ Hz, H-6_{endo}), 6-exo cycloadduct 6.66 (dd, 1H, $J_{4,7} = 2.1$ Hz, $J_{1,7} = 5.7$ Hz, H-7), 5.39 (dd, 1H, $J_{1,6} = 1.4$ Hz, $J_{1,7} = 5.7$ Hz, H-1), 3.79 (dd, 1H, $J_{4,7} = 2.1$ Hz, $J_{4,5endo} = 2.6$ Hz, $J_{4,5exo} = 5.0$ Hz, H-4), 2.97 (ddd, 1H, $J_{1,6} = 1.4$ Hz, $J_{6,5endo} = 9.5$ Hz, $J_{6,5exo} = 5.3$ Hz, H-6), 2.48 (m, 1H, H-5_{exo}), 2.29 (m, 1H, H-5_{endo}); ¹³C NMR 5-endo cycloadduct 167.5 (C-3), 133.2 (C-7), 124.7 (C-8), 118.2 (CN), 74.2 (C-1), 52.0 (C-4), 32.0 (C-6), 23.5 (C-5), 6-exo cycloadduct 168.7 (C-3), 130.3 (C-7), 120.6 (C-8), 118.3 (CN), 74.6 (C-1), 49.8 (C-4), 29.0 (C-6), 25.4 (C-5); IR 3092, 2952, 2924, 2852, 2245, 1761, 1618, 1448, 1358, 1262, 1187, 1134, 1043, 1017, 987, 850, 683 cm⁻¹.

8-Bromo-5_{exo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.75 (dd, 1H, $J_{4,7} = 2.0$ Hz, $J_{1,7} = 5.6$ Hz, H-7), 5.32 (ddd, 1H, $J_{1,6endo} = 1.7$ Hz, $J_{1,6exo} = 3.6$ Hz, $J_{1,7} = 5.6$ Hz, H-1), 3.94 (t, 1H, $J = 2.2$ Hz, H-4), 3.01 (ddd, 1H, $J_{4,5} = 2.3$ Hz, $J_{5,6exo} = 5.5$ Hz, $J_{5,6endo} = 10.7$ Hz, H-5), 2.50 (ddd, 1H, $J_{1,6exo} = 3.6$ Hz, $J_{5,6exo} = 5.5$ Hz, $J_{6exo,6endo} = 13.9$ Hz, H-6_{exo}), 2.26 (ddd, 1H, $J_{1,6endo} = 1.7$ Hz, $J_{5,6endo} = 10.7$ Hz, $J_{6exo,6endo} = 13.9$ Hz, H-6_{endo}); IR 2951, 2918, 2846, 2242, 1765, 1616, 1454, 1360, 1314, 1282, 1187, 1130, 1040, 1018, 988, 851, 812 cm⁻¹; m/z 229 (9, M⁺ for ⁸¹Br), 227 (10, M⁺ for ⁷⁹Br), 185 [70, (M⁺ for ⁸¹Br)-CO₂], 184 (11), 183 [73, (M⁺ for ⁷⁹Br)-CO₂], 176 [20, (M⁺ for ⁸¹Br)-53, retro Diels-Alder], 174 [22, (M⁺ for ⁷⁹Br)-53, retro Diels-Alder], 167 (19), 153 (17), 148 (22), 147 (29), 145 (36), 113 (10), 105 (41), 104 [100, M⁺-CO₂-Br], 103 (17), 102 (12), 93 (14), 85 (10), 78 (18), 77

(96), 75 (12), 71 (12), 67 (10), 57 (11), 51 (5); HRMS calcd for $C_8H_7^{81}BrNO_2$ (MH^+): 229.96342; found: 229.96393.

Cycloaddition of 4-Iodo-2(H)-pyran-2-one and Acrylonitrile

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 4-Iodo-2(H)-pyran-2-one **15** (45 mg, 0.2 mmol), acrylonitrile (0.5 mL, 7.6 mmol, 38 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 50 °C for 15 days then at 70 °C for 17 days. The tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of three cycloadducts and unreacted starting material (ca 14%). Silica gel chromatography, using 20% v/v ethyl acetate in petroleum ether, afforded a pure sample of the 6-*endo* isomer as well as a mixed sample of 5-*endo* and 6-*exo* cycloadducts. Combined isolated yield of cycloadducts was 35 mg, 63%.

8-Iodo-6-*endo*-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 138 °C; 1H NMR 7.10 (dd, 1H, $J_{4,7} = 1.5$ Hz, $J_{1,7} = 5.1$ Hz, H-7), 5.27 (dd, 1H, $J_{1,6} = 3.6$ Hz, $J_{1,7} = 5.1$ Hz, H-1), 3.86 (m, 1H, H-4), 3.34 (ddd, 1H, $J_{1,6} = 3.9$ Hz, $J_{5endo,6} = 5.3$ Hz, $J_{5exo,6} = 9.4$ Hz, H-6), 2.40 (ddd, 1H, $J_{4,5exo} = 3.0$ Hz, $J_{5exo,6} = 9.4$ Hz, $J_{5exo,5endo} = 13.4$ Hz, H-5_{exo}), 2.01 (ddd, 1H, $J_{4,5endo} = 2.4$ Hz, $J_{5endo,6} = 5.3$ Hz, $J_{5endo,5exo} = 13.4$ Hz, H-5_{endo}); ^{13}C NMR 169.1 (C-3), 138.3 (C-7), 118.3 (CN), 94.9 (C-8), 74.3 (C-1), 52.8 (C-4), 28.6 (C-6), 26.4 (C-5); IR 2946, 2242, 1763, 1451, 1357, 1240, 1209, 1144, 1065, 1035, 1006, 988, 961, 924, 840, 809 cm^{-1} ; m/z 276 (5), 275 (37, M^+), 231 (16, $M^+ - CO_2$), 222 [100, ($M^+ - 53$, retro Diels-Alder)], 194 (22), 104 [38, ($M^+ - CO_2 - I$)], 95 (20), 77 (24), 51 (9), 50 (5); HRMS calcd for $C_8H_7INO_2$ (MH^+): 275.95158; found: 275.95210.

8-Iodo-5_{endo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene and **8-Iodo-6_{exo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene** ¹H NMR 5-endo cycloadduct 6.97 (dm, 1H, $J_{1,7} = 5.0$ Hz, H-7), 5.21 (m, 1H, H-1), 4.05 (m, 1H, H-4), 3.28 (dt, 1H, $J_{4,5} = 3.1$ Hz, $J_{5,6endo} = 3.1$ Hz, $J_{5,6exo} = 9.4$ Hz, H-5), 2.63 (ddd, 1H, $J_{1,6exo} = 3.3$ Hz, $J_{5,6exo} = 9.4$ Hz, $J_{6exo,6endo} = 13.9$ Hz, H-6_{exo}), 2.04 (dm, 1H, $J_{6exo,6endo} = 13.9$ Hz, H-6_{endo}), 6-exo cycloadduct 7.20 (dm, 1H, $J_{1,7} = 5.0$ Hz, H-7), 5.27 (dm, 1H, $J_{1,7} = 5.0$ Hz, H-1), 3.86 (m, 1H, H-4), 2.94 (ddd, 1H, $J_{1,6} = 1.3$ Hz, $J_{5exo,6} = 4.2$ Hz, $J_{5endo,6} = 10.1$ Hz, H-6), 2.48 (m, 1H, H-5_{exo}), 2.22 (m, 1H, H-5_{endo}); ¹³C NMR 5-endo cycloadduct 167.5 (C-3), 139.1 (C-7), 118.3 (CN), 89.3 (C-8), 75.0 (C-1), 54.0 (C-4), 28.8 (C-5), 25.2 (C-6), 6-exo cycloadduct 168.7 (C-3), 142.2 (C-7), 118.1 (CN), 89.3 (C-8), 74.8 (C-1), 54.7 (C-4), 31.8 (C-6), 23.3 (C-5); IR 3077, 2952, 2924, 2852, 2246, 1761, 1599, 1450, 1355, 1295, 1246, 1205, 1173, 1061, 1037, 1018, 977, 901, 845, 808, 706, 595, 533 cm⁻¹; m/z 276 (8, MH⁺), 275 (66, M⁺), 231 [50, (M⁺-CO₂)], 222 [46, (M⁺-53, retro Diels-Alder)], 194 (20), 148 (20), 105 (12), 104 [100, (M⁺-CO₂-I)], 78 (17), 77 (57), 71 (14), 69 (11), 57 (21), 55 (14).

Cycloaddition of 4-Bromo-2(H)-pyran-2-one and Vinylene Carbonate

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 4-bromo-2(H)-pyran-2-one **14** (54 mg, 0.31 mmol), vinylene carbonate (0.2 mL, mmol, equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 5 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Purification by silica gel chromatography, using 20% v/v ethyl acetate in petroleum ether gave 5 mg (7%) of *endo* isomer cycloadduct together with unreacted starting material (ca 37%).

Endo cycloadduct m.p. 140-144 °C (dec); $^1\text{H NMR}$ 6.79 (dd, 1H, $J_{4,7} = 2.2$ Hz, $J_{1,7} = 5.6$ Hz, H-7), 5.46 (dd, 1H, $J_{1,6} = 4.0$ Hz, $J_{1,7} = 5.6$ Hz, H-1), 5.15 (dd, 1H, $J_{4,5} = 3.8$ Hz, $J_{5,6} = 7.5$ Hz, H-5), 5.10 (dd, 1H, $J_{1,6} = 4.0$ Hz, $J_{5,6} = 7.5$ Hz, H-6), 4.28 (dd, 1H, $J_{4,7} = 2.2$ Hz, $J_{4,5} = 3.8$ Hz, H-4); IR 3005, 2923, 2852, 1846, 1812, 1777, 1614, 1371, 1281, 1162, 1085, 1064, 999, 977, 851, 759 cm^{-1} ; m/z (EI) 262 (6, M^+ for ^{81}Br), 260 (6, M^+ for ^{79}Br), 218 (4, $\text{M}^+ - \text{CO}_2$), 216 (5, $\text{M}^+ - \text{CO}_2$), 176 (96, $\text{M}^+ - 86$, retro Diels-Alder), 174 (100, $\text{M}^+ - 86$, retro Diels-Alder), 147 (27), 145 (28), 127 (4), 125 (6), 95 (5), 86 (7), 83 (7), 67 (8), 65 (8), 57 (8).

Cycloaddition of 3-Chloro-2(H)-pyran-2-one and Methyl Acrylate

A sealed pressure tube (purchased from Aldrich Chemical Co Cat No Z18, 109-9) was charged with 3-chloro-2(H)-pyran-2-one **10** (94 mg, 0.72 mmol), methyl acrylate (0.5 mL, 5.6 mmol, 8 equiv), a few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two isomers of cycloadducts. Pure samples of the 5-*endo* and 6-*endo* cycloadducts were obtained by silica gel chromatography using 20% v/v ethyl acetate in petrol ether. Combined isolated yield of cycloadducts was 85 mg, 55%.

Methyl 4-chloro-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5-*endo*-carboxylate m.p. 116 °C; $^1\text{H NMR}$ 6.57 (dd, 1H, $J_{1,7} = 5.2$ Hz, $J_{7,8} = 8.0$ Hz, H-7), 6.48 (dm, 1H, $J_{7,8} = 8.0$ Hz, H-8), 5.31 (m, 1H, H-1), 3.54 (s, 3H, CO_2CH_3), 3.17 (ddd, 1H, $J_{1,5} = 0.8$ Hz, $J_{5,6\text{endo}} = 4.2$ Hz, $J_{5,6\text{exo}} = 10.0$ Hz, H-5), 2.73 (ddd, 1H, $J_{1,6\text{exo}} = 4.1$ Hz, $J_{5,6\text{exo}} = 10.0$ Hz, $J_{6\text{exo},6\text{endo}} = 13.4$ Hz, H-6_{exo}), 1.98 (ddd, 1H, $J_{1,6\text{endo}} = 1.2$ Hz, $J_{5,6\text{endo}} = 4.2$ Hz, $J_{6\text{endo},6\text{exo}} = 13.4$ Hz, H-6_{endo}); $^{13}\text{C NMR}$ 171.0 ($\underline{\text{C}}\text{O}_2\text{CH}_3$), 168.3 (C-3), 135.6 (C-7), 131.1

(C-8), 73.7 (C-1), 67.0 (C-4), 53.1 (CO₂CH₃), 44.4 (C-5), 33.8 (C-6); IR 3087, 3055, 2961, 2926, 2854, 1768, 1737, 1455, 1437, 1362, 1264, 1214, 1181, 1168, 1063, 1042, 997, 950, 939, 870, 844, 805, 741, 705, 651, 618, 585 cm⁻¹; m/z 219 (6), 218 (4), 217 (14, MH⁺), 185 [2, (M⁺-OMe)], 172 [28, (M⁺-CO₂)], 157 [8, (M⁺-CO₂Me)], 137 [32, (M⁺-CO₂-Cl)], 115 (30), 114 (20), 113 [100, (M⁺-CO₂-CO₂Me)], 112 (46), 105 (30), 102 (9), 93 (15), 78 (24), 77 (96), 65 (8), 59 (12), 55 (5), 51 (17), 50 (9); HRMS calcd for C₉H₉³⁵ClO₄Na: 239.00816; found: 239.00941.

Methyl 4-chloro-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-6_{endo}-carboxylate m.p. 60 °C; ¹H NMR 6.49 (dd, 1H, J_{1,8} = 1.7 Hz, J_{7,8} = 8.0 Hz, H-8), 6.41 (dd, 1H, J_{1,7} = 4.9 Hz, J_{7,8} = 8.0 Hz, H-7), 5.42 (ddd, 1H, J_{1,8} = 1.7 Hz, J_{1,6} = 3.9 Hz, J_{1,7} = 4.9 Hz, H-1), 3.67 (s, 3H, CO₂CH₃), 3.42 (ddd, 1H, J_{1,6} = 3.9 Hz, J_{6,5endo} = 5.9 Hz, J_{6,5exo} = 9.2 Hz, H-6), 2.43 (dd, 1H, J_{5exo,6} = 9.2 Hz, J_{5exo,5endo} = 12.7 Hz, H-5_{exo}), 2.37 (dd, 1H, J_{5endo,6} = 5.9 Hz, J_{5endo,5exo} = 12.7 Hz, H-5_{endo}); ¹³C NMR ppm 170.4 (CO₂CH₃), 169.1 (C-3), 138.8 (C-8), 130.0 (C-7), 73.8 (C-1), 64.8 (C-4), 53.2 (CO₂CH₃), 44.8 (C-6), 34.6 (C-5); IR 3081, 2952, 2922, 2852, 1780, 1738, 1436, 1364, 1306, 1259, 1205, 1116, 1057, 1025, 969, 927, 799, 714 cm⁻¹; m/z 219 (7), 218 (6), 217 (10, MH⁺), 185 [10, (M⁺-OMe)], 172 [25, (M⁺-CO₂)], 157 [6, (M⁺-CO₂Me)], 137 [15, (M⁺-CO₂-Cl)], 115 (32), 114 (20), 113 [100, (M⁺-CO₂,CO₂Me)], 112 (43), 102 (9), 78 (12), 77 (73), 65 (7), 55 (12), 51 (11); HRMS calcd for C₉H₉³⁵ClO₄Na: 239.00816; found: 239.00752.

Cycloaddition of 3-Bromo-2(H)-pyran-2-one and Methyl Acrylate

A sealed pressure tube (purchased from Aldrich Chemical Co Cat No Z18, 109-9) was charged with 3-bromo-2(H)-pyran-2-one **4** (70mg, 0.40 mmol), methyl acrylate (0.6 mL, 6.7 mmol, 17 equiv), a few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and immersed in an oil bath maintained at 100 °C. After 3

days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two isomers of cycloadducts. Pure samples of the 5-*endo* and 6-*endo* cycloadducts were obtained by silica gel chromatography using 20% v/v ethyl acetate in petrol ether. Combined isolated yield of cycloadducts was 82 mg, 80%.

Methyl 4-bromo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5-*endo*-carboxylate m.p. 99-100 °C; ¹H NMR 6.59 (d, 1H, J_{7,8} = 8.0 Hz, H-8), 6.49 (dd, 1H, J_{1,7} = 5.2 Hz, J_{7,8} = 8.0 Hz, H-7), 5.32 (m, 1H, H-1), 3.76 (s, 3H, CO₂CH₃), 3.24 (dd, 1H, J_{5,6endo} = 4.2 Hz, J_{5,6exo} = 9.7 Hz, H-5), 2.73 (ddd, 1H, J_{1,6exo} = 4.1 Hz, J_{5,6exo} = 9.7 Hz, J_{6exo,6endo} = 13.7 Hz, H-6_{exo}), 1.98 (ddd, 1H, J_{1,6endo} = 1.0 Hz, J_{5,6endo} = 4.2 Hz, J_{6endo,6exo} = 13.7 Hz, H-6_{endo}); ¹³C NMR 171.29 (CO₂CH₃), 167.8 (C-3), 136.6 (C-8), 131.3 (C-7), 73.8 (C-1), 58.5 (C-4), 53.0 (CO₂CH₃), 45.2 (C-5), 34.2 (C-6); IR 2955, 2923, 2852, 1759, 1738, 1436, 1362, 1281, 1209, 1164, 1125, 1060, 1009, 992, 948, 865, 843, 787, 701 cm⁻¹; m/z 263 (4, MH⁺ for ⁸¹Br), 261 (4, MH⁺ for ⁷⁹Br), 231 (8), 229 (8), 218 [3, (MH⁺ for ⁸¹Br-CO₂)], 216 [3, (MH⁺ for ⁷⁹Br-CO₂)], 176 [8, (MH⁺ for ⁸¹Br -86, retro Diels-Alder)], 174 [9, (MH⁺ for ⁷⁹Br -86, retro Diels-Alder)], 159 [44, (MH⁺ for ⁸¹Br-CO₂-CO₂Me)], 158 (17), 157 [45, MH⁺ (for ⁷⁹Br)-CO₂-CO₂Me], 156 (14), 137 [82, (M⁺-CO₂-Br)], 105 (18), 93 (57), 78 (60), 77 (100), 59 (18), 55 (33), 51 (17), 39 (13); HRMS calcd for C₉H₉⁸¹BrO₄Na: 284.95559; found: 284.95427; Anal. calcd for C₉H₉BrO₄: C, 41.41, H, 3.47; found: C, 41.32, H, 3.65.

Methyl 4-bromo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-6-*endo*-carboxylate m.p. 172 °C; ¹H NMR 6.68 (dd, 1H, J_{1,8} = 1.6 Hz, J_{7,8} = 8.0 Hz, H-8), 6.42 (dd, 1H, J_{1,7} = 5.0 Hz, J_{7,8} = 8.0 Hz, H-7), 5.49 (dd, 1H, J_{1,8} = 1.6 Hz, J_{1,6exo} = 3.9 Hz, J_{1,7} = 5.0 Hz, H-1), 3.74 (s, 3H, CO₂CH₃), 3.49 (ddd, 1H, J_{1,6} = 3.9 Hz, J_{6,5endo} = 5.5 Hz, J_{6,5exo} = 9.5 Hz, H-6), 2.61 (dd, 1H, J_{5exo,6} = 9.5 Hz, J_{5exo,5endo} = 12.7 Hz, H-

5_{exo}), 2.53 (dd, 1H, $J_{5\text{endo},6} = 5.5$ Hz, $J_{5\text{endo},5\text{exo}} = 12.7$ Hz, H-5_{endo}); ^{13}C NMR 170.4 (CO_2CH_3), 169.1 (C-3), 139.7 (C-8), 130.3 (C-7), 73.9 (C-1), 55.8 (C-4), 53.2 (CO_2CH_3), 45.4 (C-6), 35.9 (C-5); IR 3082, 2955, 2918, 2846, 1777, 1738, 1437, 1364, 1306, 1253, 1206, 1149, 1120, 1065, 1049, 1015, 965, 925, 858, 826, 789, 771, 714, 659 cm^{-1} ; m/z 263 [5, MH^+ (for ^{81}Br)], 261 [5, MH^+ (for ^{79}Br)], 231 (12), 229 (12), 218 [11, (MH^+ for ^{81}Br)- CO_2], 216 [11, (MH^+ for ^{81}Br)- CO_2], 176 [14, (MH^+ for ^{81}Br)-86, retro Diels-Alder], 174 [15, (MH^+ for ^{79}Br)-86, retro Diels-Alder], 159 [72, (MH^+ for ^{81}Br)- CO_2 - CO_2Me], 158 (31), 157 (74, (MH^+ for ^{79}Br)- CO_2 , CO_2Me), 156 (27), 137 (64, M^+ - CO_2 , Br), 105 (12), 93 (44), 78 (73), 77 (100), 59 (16), 55 (66), 51 (21), 39 (17); HRMS calcd for $\text{C}_9\text{H}_9^{81}\text{BrO}_4\text{Na}$: 284.95559 ; found: 284.95405.

Cycloaddition of 3-Iodo-2(H)-pyran-2-one and Methyl Acrylate

A sealed pressure tube (purchased from Aldrich Chemical Co Cat No Z18, 109-9) was charged with 3-iodo-2(H)-pyran-2-one **11** (44 mg, 0.198 mmol), methyl acrylate (0.5 mL, 5.6 mmol, 28 equiv), a few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and immersed in an oil bath maintained at 90 °C. After 4 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two isomers of cycloadducts. Pure samples of the 5-*endo* and 6-*endo* cycloadducts were obtained by silica gel chromatography using 20% v/v ethyl acetate in petrol ether. Combined isolated yield of cycloadducts was 48 mg, 74%.

Methyl 4-iodo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5_{endo}-carboxylate. m.p. 76 °C; ^1H NMR 6.73 (dd, 1H, $J_{1,8} = 1.2$ Hz, $J_{7,8} = 8.0$ Hz, H-8), 6.31 (dd, 1H, $J_{1,7} = 5.3$ Hz, $J_{7,8} = 8.0$ Hz, H-7), 5.32 (ddt, 1H, $J_{1,6\text{endo}} = 1.5$ Hz, $J_{1,6\text{exo}} = 4.0$ Hz, $J_{1,7} = 5.3$ Hz, H-1), 3.77 (s, 3H, CO_2CH_3), 3.28 (dd, 1H, $J_{5,6\text{endo}} = 4.3$ Hz, $J_{5,6\text{exo}} = 9.6$ Hz, H-5), 2.69 (ddd, 1H, $J_{1,6\text{exo}} = 4.0$ Hz, $J_{5,6\text{exo}} = 9.6$ Hz, $J_{6\text{endo},6\text{exo}} =$

13.2 Hz, H-6_{exo}), 1.97 (ddd, 1H, $J_{1,6\text{endo}} = 1.5$ Hz, $J_{5,6\text{endo}} = 4.3$ Hz, $J_{6\text{endo},6\text{exo}} = 13.2$ Hz, H-6_{endo}); ¹³C NMR 171.8 (C=O₂CH₃), 168.2 (C-3), 139.4 (C-8), 131.4 (C-7), 73.9 (C-1), 53.0 (CO₂CH₃), 47.1 (C-5), 37.0 (C-4), 34.2 (C-6); IR 3080, 2956, 2923, 2852, 1738, 1646, 1463, 1434, 1363, 1278, 1249, 1206, 1175, 1159, 1124, 1057, 1032, 1004, 972, 950, 883, 864, 841, 787, 734, 701, 652, 609, 586 cm⁻¹; m/z 309 (5), 308 (10, M⁺), 277 (9), 264 [6, (M⁺-CO₂)], 205 [26, (M⁺-CO₂-CO₂Me)], 204 (13), 137 [64, (M⁺-CO₂-I)], 105 (15), 95 (3), 94 (8), 93 (70), 91 (11), 79 (11), 78 (100), 77 (29), 59 (28), 55 (28), 51 (11), 39 (13); HRMS calcd for C₉H₉IO₄Na: 330.94377; found: 330.94358; Anal. calcd for C₉H₉IO₄: C, 35.09, H, 2.94; found: C, 35.24, H, 2.78.

Methyl 4-iodo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-6_{endo}-carboxylate. m.p. 68 °C; ¹H NMR 6.84 (dd, 1H, $J_{1,8} = 1.9$ Hz, $J_{7,8} = 7.9$ Hz, H-8), 6.25 (dd, 1H, $J_{1,7} = 5.3$ Hz, $J_{7,8} = 7.9$ Hz, H-7), 5.50 (ddd, 1H, $J_{1,8} = 1.9$ Hz, $J_{1,6} = 3.9$ Hz, $J_{1,7} = 5.3$ Hz, H-1), 3.73 (s, 3H, CO₂CH₃), 3.47 (ddd, 1H, $J_{1,6} = 3.9$ Hz, $J_{6,5\text{endo}} = 5.4$ Hz, $J_{5\text{exo},6} = 9.6$ Hz, H-6), 2.72 (dd, 1H, $J_{5\text{exo},6} = 9.6$ Hz, $J_{5\text{endo},5\text{exo}} = 13.0$ Hz, H-5_{exo}), 2.61 (dd, 1H, $J_{5\text{endo},6} = 5.4$ Hz, $J_{5\text{endo},5\text{exo}} = 13.0$ Hz, H-5_{endo}); ¹³C NMR 170.4 (C=O₂CH₃), 168.9 (C-3), 142.4 (C-8), 130.7 (C-7), 73.8 (C-1), 53.2 (CO₂CH₃), 46.2 (C-6), 38.9 (C-5), 33.0 (C-4); IR 3076, 2953, 2863, 1770, 1737, 1436, 1365, 1305, 1205, 1118, 1060, 1010, 959, 922, 713 cm⁻¹; m/z (CI) 326 [100, (MNH₄⁺)], 277 (7), 264 [25, (M⁺-CO₂)], 205 [33, (M⁺-CO₂-CO₂Me)], 204 (14), 137 [10, (M⁺-CO₂-I)], 105 (4), 95 (3), 94 (4), 93 (26), 91 (4), 79 (8), 78 (100), 77 (16), 59 (12), 55 (35), 51 (9), 39 (10); HRMS calcd for C₉H₉IO₄Na: 330.94377; found: 330.94366.

Cycloaddition of 3-Chloro-2(H)-pyran-2-one and Acrylonitrile

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 3-chloro-2(H)-pyran-2-one **10** (62 mg, 0.48 mmol), acrylonitrile (0.6 mL, 9.1 mmol, 19 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic

stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Pure sample of the 5-endo, 5-exo, 6-endo and 6-exo cycloadducts were obtained by silica gel chromatography, using 10-60% v/v ethyl acetate in petroleum ether. Combined isolated yield of cycloadducts was 75.5 mg, 86%.

4-Chloro-6-endo-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ^1H NMR 6.74 (ddd, 1H, $J_{5\text{exo},8} = 0.8$ Hz, $J_{1,8} = 1.9$ Hz, $J_{7,8} = 8.0$ Hz, H-8), 6.66 (dd, 1H, $J_{1,7} = 5.0$ Hz, $J_{7,8} = 8.0$ Hz, H-7), 5.44 (ddd, 1H, $J_{1,8} = 1.9$ Hz, $J_{1,6\text{exo}} = 3.8$ Hz, $J_{1,7} = 5.0$ Hz, H-1), 3.52 (ddd, 1H, $J_{1,6} = 3.8$ Hz, $J_{5\text{endo},6} = 5.1$ Hz, $J_{5\text{exo},6} = 9.6$ Hz, H-6), 2.68 (dd, 1H, $J_{5\text{exo},8} = 0.8$ Hz, $J_{5\text{exo},6} = 9.7$ Hz, $J_{5\text{exo},5\text{endo}} = 13.0$ Hz, H-5exo), 2.33 (dd, 1H, $J_{5\text{endo},6} = 5.1$ Hz, $J_{5\text{exo},5\text{endo}} = 13.0$ Hz, H-5endo); ^{13}C NMR 166.8 (C-3), 139.5 (C-8), 129.2 (C-7), 117.2 (CN), 72.1 (C-1), 63.2 (C-4), 35.5 (C-5), 29.5 (C-6); IR 2953, 2925, 2849, 2245, 1783, 1453, 1359, 1297, 1236, 1193, 1151, 1123, 1085, 1057, 1024, 1007, 972, 958, 892, 859, 802, 773, 726, 660, 519 cm^{-1} ; m/z 183 (10, M^+), 141 (6), 139 [18, ($\text{M}^+ - \text{CO}_2$)], 130 [15, ($\text{M}^+ - 53$, retro Diels-Alder)], 105 (13), 104 (100, $\text{M}^+ - \text{CO}_2 - \text{Cl}$), 102 (20), 77 (32); HRMS calcd for $\text{C}_8\text{H}_6^{35}\text{ClNO}_2\text{Na}$: 205.99793; found: 205.99795.

4-Chloro-5-endo-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 128 °C; ^1H NMR 6.75 (dd, 1H, $J_{1,7} = 5.2$ Hz, $J_{7,8} = 7.9$ Hz, H-7), 6.61 (dm, 1H, $J_{7,8} = 7.9$ Hz, H-8), 5.37 (ddd, 1H, $J_{1,6\text{endo}} = 1.6$ Hz, $J_{1,6\text{exo}} = 3.6$ Hz, $J_{1,7} = 5.2$ Hz, H-1), 3.39 (dd, 1H, $J_{5,6\text{endo}} = 3.3$ Hz, $J_{5,6\text{exo}} = 9.7$ Hz, H-5), 2.84 (ddd, 1H, $J_{1,6\text{exo}} = 3.6$ Hz, $J_{5,6\text{exo}} = 9.7$ Hz, $J_{6\text{exo},6\text{endo}} = 13.9$ Hz, H-6_{exo}), 2.20 (ddd, 1H, $J_{1,6\text{endo}} = 1.6$ Hz, $J_{5,6\text{endo}} = 3.3$ Hz, $J_{6\text{exo},6\text{endo}} = 13.9$ Hz, H-6_{endo}); ^{13}C NMR 166.1 (C-3), 135.6 (C-7), 132.8 (C-8), 117.4 (CN), 72.3 (C-1), 65.3 (C-4), 33.5 (C-5), 33.4 (C-6); IR 3097, 2955, 2247, 1767, 1439, 1362, 1312, 1279, 1173, 1127, 1069, 1018, 976, 890, 872, 748, 716, 698, 616, 615 cm^{-1} ; m/z 185 (20), 184 (7), 183

(20, M⁺), 139 [59, (M⁺-CO₂)], 132 (14), 130 [41, (M⁺-53, retro Diels-Alder)], 105 (19), 104 (100, M⁺-CO₂-Cl), 103 (14), 102 (35), 99 (14), 95 (3), 78 (12), 77 (66); HRMS calcd for C₈H₆³⁵ClNO₂Na: 205.99793; found: 205.99796.

4-Chloro-6_{exo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.61 (dd, 1H, J_{1,8} = 1.8 Hz, J_{7,8} = 8.0 Hz, H-8), 6.54 (dd, 1H, J_{1,7} = 5.0 Hz, J_{7,8} = 8.0 Hz, H-7), 5.43 (dt, 1H, J_{1,6} = J_{1,8} = 1.7 Hz, J_{1,7} = 5.0 Hz, H-1), 3.08 (ddd, 1H, J_{1,6} = 1.4 Hz, J_{5_{exo},6} = 6.1 Hz, J_{5_{endo},6} = 9.0 Hz, H-6), 2.50 (m, 2H, H-5); ¹³C NMR 166.2 (C-3), 138.8 (C-8), 129.8 (C-7), 117.5 (CN), 73.0 (C-1), 63.1 (C-4), 34.4 (C-5), 20.94 (C-6); IR 3087, 2952, 2925, 2857, 2246, 1780, 1455, 1360, 1261, 1062, 1028, 928, 800, 706 cm⁻¹; m/z 185 (5), 183 (5, M⁺), 139 [18, (M⁺-CO₂)], 130 [15, (M⁺-53, retro Diels-Alder)], 105 (10), 104 [100, M⁺-CO₂-Cl], 102 (20), 95 [5, (130-Cl)], 77 (24), 51 (14); HRMS calcd for C₈H₆³⁵ClNO₂Na: 205.99793; found: 205.99796.

4-Chloro-5_{exo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p.135 °C; ¹H NMR 6.67 (dd, 1H, J_{1,7} = 5.1 Hz, J_{7,8} = 8.0 Hz, H-7), 6.52 (dd, 1H, J_{1,8} = 1.8 Hz, J_{7,8} = 8.0 Hz, H-8), 5.37 (ddm, 1H, J_{1,6_{exo}} = 3.8 Hz, J_{1,7} = 5.1 Hz, H-1), 3.20 (dd, 1H, J_{5,6_{exo}} = 5.2 Hz, J_{5,6_{endo}} = 11.0 Hz, H-5), 2.70 (ddd, 1H, J_{1,6_{exo}} = 4.1 Hz, J_{5,6_{exo}} = 5.2 Hz, J_{6_{exo},6_{endo}} = 13.7 Hz, H-6_{exo}), 2.40 (ddd, 1H, J_{1,6_{endo}} = 1.5 Hz, J_{5,6_{endo}} = 11.0 Hz, J_{6_{exo},6_{endo}} = 13.7 Hz, H-6_{endo}); ¹³C NMR 165.3 (C-3), 136.0 (C-8), 133.2 (C-7), 116.9 (CN), 72.4 (C-1), 65.4 (C-4), 33.9 (C-5), 33.1 (C-6); IR 2953, 2925, 2849, 2236, 1755, 1359, 1344, 1316, 1274, 1259, 1193, 1146, 1132, 1061, 1033, 1011, 996, 979, 946, 885, 800, 780, 701, 637, 607, 594 cm⁻¹; m/z 183 (13, M⁺), 141 (11), 139 [31, (M⁺-CO₂)], 130 [13, (M⁺-53, retro Diels-Alder)], 105 (10), 104 (100, M⁺-CO₂-Cl), 102 (15), 77 (30); HRMS calcd for C₈H₆³⁵ClNO₂Na: 205.99793; found: 205.99796.

Cycloaddition of 3-Bromo-2(H)-pyran-2-one and Acrylonitrile

A sealed pressure tube (purchased from Aldrich Chemical Co Cat No Z18, 109-9) was charged with 3-bromo-2(H)-pyran-2-one **4** (96 mg, 0.55 mmol), acrylonitrile (0.6 mL, 9.1 mmol, 17 equiv), a few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of four cycloadducts. Pure sample of the 5-*endo*, 5-*exo*, 6-*endo* and 6-*exo* cycloadducts were obtained by silica gel chromatography, using 10-60% v/v ethyl acetate in petroleum ether. Combined isolated yield of cycloadducts was 97 mg, 78%.

4-Bromo-5_{endo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 129 °C; ¹H NMR 6.72 (dd, 1H, J_{1,8} = 1.6 Hz, J_{7,8} = 8.0 Hz, H-8), 6.67 (dd, 1H, J_{1,7} = 5.2 Hz, J_{7,8} = 8.0 Hz, H-7), 5.37 (ddt, 1H, J_{1,8} = 1.6 Hz, J_{1,6endo} = 1.6 Hz, J_{1,6exo} = 3.6 Hz, J_{1,7} = 5.2 Hz, H-1), 3.46 (dd, 1H, J_{5,6endo} = 3.2 Hz, J_{5,6exo} = 9.6 Hz, H-5), 2.84 (ddd, 1H, J_{1,6exo} = 3.6 Hz, J_{5,6exo} = 9.6 Hz, J_{6exo,6endo} = 3.8 Hz, H-6_{exo}), 2.22 (ddd, 1H, J_{1,6endo} = 1.6 Hz, J_{5,6endo} = 3.2 Hz, J_{6exo,6endo} = 3.8 Hz, H-6_{endo}); ¹³C NMR 166.6 (C-3), 139.7 (C-8), 133.6 (C-7), 119.3 (CN), 72.8 (C-1), 37.2 (C-5), 34.7 (C-4), 34.9 (C-6); IR 3087, 2953, 2248, 1766, 1445, 1361, 1276, 1168, 1127, 1068, 1009, 973, 872, 711, 695 cm⁻¹; m/z 185 (18, M⁺-CO₂ for ⁸¹Br), 183 (18, M⁺-CO₂ for ⁷⁹Br), 176 [8, (M⁺-53 for ⁸¹Br, retro Diels-Alder)], 174 [8, (M⁺-53 for ⁷⁹Br, retro Diels-Alder)], 147 (9), 145 (9), 105 (10), 104 [100, (M⁺-CO₂-Br)], 103 (6), 78 (9), 77 (36), 57 (11), 51 (12); Anal. calcd for C₈H₆BrNO₂: C, 42.21, H, 2.65, N, 6.14; found: C, 42.32, H, 2.63, N, 6.23.

4-Bromo-6_{endo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.85 (dd, 1H, J_{1,8} = 1.2 Hz, J_{7,8} = 8.0 Hz, H-8), 6.41 (dd, 1H, J_{1,7} = 4.9 Hz, J_{7,8} = 8.0 Hz, H-7), 5.44 (ddd, 1H, J_{1,8} = 1.2 Hz, J_{1,6} = 3.7

Hz, $J_{1,7} = 4.9$ Hz, H-1), 3.52 (ddd, 1H, $J_{1,6} = 3.7$ Hz, $J_{5endo,6} = 5.0$ Hz, $J_{5exo,6} = 9.5$ Hz, H-6), 2.79 (dd, 1H, $J_{5exo,6} = 9.5$ Hz, $J_{5endo,5exo} = 13.0$ Hz, H-5_{exo}), 2.42 (dd, 1H, $J_{5endo,6} = 5.0$ Hz, $J_{5endo,5exo} = 13.0$ Hz, H-5_{endo}); ^{13}C NMR 165.5 (C-3), 140.4 (C-8), 129.5 (C-7), 117.2 (CN), 72.2 (C-1), 53.5 (C-4), 36.7 (C-5), 30.1 (C-6); IR 3082, 2952, 2926, 2852, 2249, 1778, 1452, 1366, 1300, 1262, 1152, 1120, 1085, 1056, 1043, 1016, 970, 954, 895, 849, 802, 784, 727, 664, 641 cm^{-1} ; m/z 185 [18, (M^+ -CO₂ for ^{81}Br)], 183 (18, M^+ -CO₂ for ^{79}Br), 176 [8, (M^+ -53 for ^{81}Br , retro Diels-Alder)], 174 [8, (M^+ -53 for ^{79}Br , retro Diels-Alder)], 147 (9), 145 (9), 105 (10), 104 (100, M^+ -CO₂-Br), 103 (6), 78 (9), 77 (36), 57 (11), 51 (12); HRMS calcd for $\text{C}_8\text{H}_7^{81}\text{BrNO}_2$ (MH^+): 229.96342; found: 229.96412.

4-Bromo-6_{exo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ^1H NMR 6.72 (dd, 1H, $J_{1,8} = 1.5$ Hz, $J_{7,8} = 8.0$ Hz, H-8), 6.47 (dd, 1H, $J_{1,7} = 5.2$ Hz, $J_{7,8} = 8.0$ Hz, H-7), 5.43 (dt, 1H, $J_{1,6} = J_{1,8} = 1.5$ Hz, $J_{1,7} = 5.2$ Hz, H-1), 3.05 (ddd, 1H, $J_{1,6} = 1.4$ Hz, $J_{5exo,6} = 5.5$ Hz, $J_{5endo,6} = 9.5$ Hz, H-6), 2.59 (m, 2H, H-5); ^{13}C NMR 166.3 (C-3), 139.7 (C-8), 130.1 (C-7), 117.5 (CN), 73.1 (C-1), 53.5 (C-4), 35.6 (C-5), 30.5 (C-6); IR 2953, 2924, 2245, 1774, 1453, 1359, 1222, 1165, 1123, 1052, 1024, 972, 920, 873, 849, 811, 778, 736, 703 cm^{-1} , m/z 229 (3), 228 (3), 227 (30), 185 [33, (M^+ for ^{81}Br)-CO₂], 183 (35, (M^+ for ^{79}Br)-CO₂), 176 [9, (M^+ for ^{81}Br)-53, retro Diels-Alder], 174 [9, (M^+ for ^{79}Br)-53, retro Diels-Alder], 148 (11), 147 (6), 145 (6), 137 (14), 136 (12), 129 (11), 127 (10), 125 (13), 123 (11), 113 (12), 111 (19), 105 (19), 104 (100, M^+ -CO₂-Br), 99 (15), 98 (13), 97 (26), 96 (11), 95 (11), 85 (23), 84 (15), 83(19), 82 (13), 81 (17), 77 (16), 71 (26), 70 (13), 69 (17), 57 (27); HRMS calcd for $\text{C}_8\text{H}_7^{81}\text{BrNO}_2$ (MH^+): 229.96342; found: 229.96385.

4-Bromo-5_{exo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p.138 °C; ^1H NMR 6.65 (dd, 1H, $J_{1,8} = 1.9$ Hz, $J_{7,8} = 8.0$ Hz, H-8), 6.59 (dd, 1H, $J_{1,7} = 5.0$ Hz, $J_{7,8} = 8.0$ Hz, H-7), 5.37 (ddt, 1H, $J_{1,8} = J_{1,6endo} = 1.7$ Hz, $J_{1,6exo} = 3.7$ Hz, $J_{1,7} = 5.0$ Hz, H-1), 3.25 (dd, 1H, $J_{5,6exo} = 5.1$ Hz, $J_{5,6endo} = 10.9$ Hz,

H-5), 2.73 (dt, 1H, $J_{1,6\text{exo}} = 4.5$ Hz, $J_{5,6\text{exo}} = 13.7$ Hz, H-6_{exo}), 2.37 (ddd, 1H, $J_{1,6\text{endo}} = 1.5$ Hz, $J_{5,6\text{endo}} = 10.9$ Hz, $J_{6\text{exo},6\text{endo}} = 13.7$ Hz, H-6_{endo}); ¹³C NMR 164.7 (C-3), 137.0 (C-8), 133.4 (C-7), 117.4 (CN), 72.5 (C-1), 56.4 (C-4), 34.8 (C-5), 33.5 (C-6); IR 3076, 2953, 2236, 1741, 1453, 1359, 1316, 1269, 1245, 1189, 1142, 1132, 1071, 1052, 1031, 1005, 981, 976, 943, 879, 797, 774, 698 cm⁻¹, m/z 229 (7), 228 (6), 227 (7), 225(12), 224 (10), 223 (12), 222 (13), 221 (39), 211 (13), 209 (12), 208 (10), 197 (13), 196 (12), 194 (11), 185 [22, (M⁺ for ⁸¹Br)-CO₂], 183 (29, (M⁺ for ⁷⁹Br)-CO₂], 181 (13), 180 (11), 176 [14, (M⁺ for ⁸¹Br)-53, retro Diels-Alder], 174 [14, (M⁺ for ⁷⁹Br)-53, retro Diels-Alder], 169 (12), 168 (10), 167 (13), 166 (11), 165 (13), 155 (13), 153 (17), 152 (14), 150 (13), 141 (15), 140 (10), 139 (18), 138 (15), 137 (13), 136 (10), 129 (16), 127 (19), 126 (15), 125 (27), 124(17), 123 (17), 113 (21), 112 (15), 111 (34), 110 (16), 109 (13), 105 (112), 104 (100, M⁺-CO₂-Br), 99 (21), 98 (22), 97 (39), 96 (22), 95 (14), 85 (23), 84 (29), 84 (21), 83(22), 82 (18), 81 (14), 77 (39), 73 (14), 72 (15), 71 (29), 70 (14), 69 (13), 60 (15), 59 (21), 57 (30); HRMS calcd for C₈H₇⁸¹BrNO₂ (MH⁺): 229.96342; found: 229.96380.

Cycloaddition of 3-Iodo-2(H)-pyran-2-one and Acrylonitrile

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 3-Iodo-2(H)-pyran-2-on **11** (95 mg, 0.43 mmol), acrylonitrile (0.6 mL, 9.1 mmol, 21 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of four cycloadducts. Pure sample of the 5-*endo*, 5-*exo*, 6-*endo* and 6-*exo* cycloadducts were obtained by silica gel

chromatography, using 10-60% v/v ethyl acetate in petroleum ether. Combined isolated yield of cycloadducts was 88 mg, 75%.

4-Iodo-6_{endo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 7.00 (dd, 1H, J_{1,8} = 1.8 Hz, J_{7,8} = 8.0 Hz, H-8), 6.43 (dd, 1H, J_{1,7} = 5.0 Hz, J_{7,8} = 8.0 Hz, H-7), 5.44 (ddd, 1H, J_{1,8} = 1.8 Hz, J_{1,6} = 3.8 Hz, J_{1,7} = 5.0 Hz, H-1), 3.49 (ddd, 1H, J_{1,6} = 3.8 Hz, J_{5endo,6} = 5.0 Hz, J_{5exo,6} = 9.4 Hz, H-6), 2.89 (dd, 1H, J_{5exo,6} = 9.4 Hz, J_{5endo,5exo} = 13.1 Hz, H-5_{exo}), 2.50 (dd, 1H, J_{5endo,6} = 5.0 Hz, J_{5endo,5exo} = 13.1 Hz, H-5_{endo}); ¹³C NMR 166.7 (C-3), 143.1 (C-8), 129.8 (C-7), 117.2 (CN), 72.2 (C-1), 39.6 (C-5), 30.8 (C-6), 29.8 (C-4); IR 2962, 2925, 2859, 2236, 1769, 1448, 1420, 1363, 1259, 1099, 1080, 1052, 1024, 797 cm⁻¹; m/z 275 (19, M⁺), 232 (21), 231 (97, M⁺-CO₂), 222 (4, M⁺-53, retro Diels-Alder), 194 (10), 147 (9), 109 (10), 105 (17), 104 (100, M⁺-CO₂-I), 103 (9), 97 (11), 85 (11), 78 (14), 77 (73, 104 - HCN), 71 (12), 57 (15); HRMS (ESI) calcd for C₈H₇INO₂ (MH⁺): 275.95160; found: 275.95210.

4-Iodo-5_{endo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 123 °C; ¹H NMR 6.87 (dd, 1H, J_{1,8} = 1.4 Hz, J_{7,8} = 8.0 Hz, H-8), 6.49 (dd, 1H, J_{1,7} = 5.1 Hz, J_{7,8} = 7.9 Hz, H-7), 5.37 (ddt, 1H, J_{1,8} = 1.6 Hz, J_{1,6exo} = 3.6 Hz, J_{1,7} = 5.1 Hz, H-1), 3.49 (dd, 1H, J_{5,6endo} = 3.2 Hz, J_{5,6exo} = 9.5 Hz, H-5), 2.80 (ddd, 1H, J_{1,6exo} = 3.6 Hz, J_{5,6exo} = 9.5 Hz, J_{6exo,6endo} = 13.7 Hz, H-6_{exo}), 2.21 (ddd, 1H, J_{1,6endo} = 1.6 Hz, J_{5,6endo} = 3.2 Hz, J_{6exo,6endo} = 13.7 Hz, H-6_{endo}); ¹³C NMR 166.6 (C-3), 139.7 (C-8), 133.6 (C-7), 119.3 (CN), 72.8 (C-1), 37.2 (C-5), 34.7 (C-4), 34.4 (C-6); IR 3098, 3065, 2923, 2853, 2244, 1755, 1646, 1467, 1364, 1344, 1311, 1265, 1232, 1167, 1125, 1064, 1044, 1023, 1003, 979, 965, 870, 741, 709, 600 cm⁻¹; m/z 276 (1), 275 (7, M⁺), 231 [100, (M⁺-CO₂)], 222 [5, (M⁺-53, retro Diels-Alder)], 194 (7), 127 (6, I), 104 [74, (M⁺-CO₂-I)], 95 [5, (222 - I⁺)], 78 (10), 77 (44), 51 (13), 50 (7); HRMS calcd for C₈H₆INO₂Na: 297.9335; found: 297.93352.

4-Iodo-5_{exo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 159-160 °C; ¹H NMR 6.85 (dd, 1H, J_{1,8} = 1.8 Hz, J_{7,8} = 7.9 Hz, H-8), 6.41 (dd, 1H, J_{1,7} = 5.1 Hz, J_{7,8} = 7.9 Hz, H-7), 5.38 (ddt, 1H, J_{1,6_{exo}} = 1.8 Hz, J_{1,6_{endo}} = 3.7 Hz, J_{1,7} = 5.1 Hz, H-1), 3.26 (dd, 1H, J_{5,6_{exo}} = 5.0 Hz, J_{5,6_{endo}} = 10.9 Hz, H-5), 2.76 (ddd, 1H, J_{1,6_{exo}} = 4.1 Hz, J_{5,6_{exo}} = 5.0 Hz, J_{6_{endo},6_{exo}} = 13.6 Hz, H-6_{exo}), 2.30 (ddd, 1H, J_{1,6_{endo}} = 1.4 Hz, J_{5,6_{endo}} = 10.9 Hz, J_{6_{endo},6_{exo}} = 13.6 Hz, H-6_{endo}); ¹³C NMR 165.5 (C-3), 140.2 (C-8), 134.0 (C-7), 118.1 (CN), 73.0 (C-1), 37.3 (C-6), 34.3 (C-4), 34.0 (C-5); IR 2951, 2922, 2852, 2242, 1761, 1464, 1361, 1339, 1261, 1070, 1048, 1023, 874, 801, 743, 701 cm⁻¹; m/z 275 (6, M⁺), 236 (16), 232 (11), 231 [100, (M⁺-CO₂)], 222 [8, (M⁺-53, retro Diels-Alder)], 194 (9), 127 (9, I⁺), 104 [71, (M⁺-CO₂-I)], 95 [6, (222 - I)], 78 (10), 77 (45), 59 (12), 51 (11), 50 (7); HRMS calcd for C₈H₆INO₂Na: 297.9335; found: 297.93247.

4-Iodo-6_{exo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.87 (dd, 1H, J_{1,8} = 1.8 Hz, J_{7,8} = 7.9 Hz, H-8), 6.31 (dd, 1H, J_{1,7} = 5.2 Hz, J_{7,8} = 7.9 Hz, H-7), 5.42 (dt, 1H, J_{1,6} = 1.6 Hz, J_{1,7} = 5.2 Hz, H-1), 2.98 (ddd, 1H, J_{1,6} = 1.4 Hz, J_{5_{exo},6} = 5.0 Hz, J_{5_{endo},6} = 9.9 Hz, H-6), 2.69 (m, 2H, H-5); ¹³C NMR 157.6 (C-3), 142.3 (C-8), 130.4 (C-7), 117.6 (CN), 73.1 (C-1), 31.2 (C-5), 30.0 (C-4), 29.7 (C-5); IR 2915, 2849, 2245, 1769, 1750, 1712, 1458, 1377, 1359, 1259, 1217, 1113, 1052, 1024, 962, 920, 807, 703 cm⁻¹; m/z 275 (4, M⁺), 232 (10), 231 (100, M⁺-CO₂), 222 (5, M⁺-53, retro Diels-Alder), 194 (7), 148 (11), 105 (10), 104 (84, M⁺-CO₂-I), 103 (8), 97 (14), 85 (13), 83 (13), 78 (11), 77 (47), 71 (17), 57 (24), 55 (14); HRMS calcd for C₈H₆INO₂Na: 297.93354; found: 297.93390.

Cycloaddition of 3-Chloro-2(H)-pyran-2-one and Vinylene carbonate

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 3-chloro-2(H)-pyran-2-one **10** (60 mg, 0.46 mmol), vinylene carbonate (1 mL, 15.7 mmol, 29 equiv), few

crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of one cycloadduct and unreacted starting material (ca 23%). Pure sample of the *endo* cycloadduct was obtained by silica gel chromatography, using 30% v/v ethyl acetate in petroleum ether. Isolated yield of the *endo* cycloadduct was 25 mg, 26%.

***endo* isomer**

m.p. 174 °C; ¹H NMR 6.63 (dd, 1H, J_{1,7} = 5.0 Hz, J_{7,8} = 8.0 Hz, H-7), 6.53 (dd, 1H, J_{1,8} = 1.6 Hz, J_{7,8} = 8.0 Hz, H-8), 5.51 (td, 1H, J_{1,8} = 1.6 Hz, J_{1,7} = J_{1,6} = 4.7 Hz, H-1), 5.22 (dd, 1H, J_{1,6exo} = 4.4 Hz, J_{5,6exo} = 7.7 Hz, H-6), 4.95 (d, 1H, J_{5exo,6} = 7.8 Hz, H-5); ¹³C NMR 164.0 (C-3), 152.5 (CO, carbonate), 135.9 (C-7), 129.2 (H-8), 76.8 (C-1), 73.5 (C-6), 71.6 (C-5), 67.5 (C-4); IR 3003, 2919, 2846, 1795, 1712, 1423, 1363, 1223, 1163, 1096, 1046, 946, 736 cm⁻¹; m/z 218 (6), 217 (5), 216 (6, M⁺), 176 (20), 174 (28), 172 (18, M⁺ - CO₂), 145 (17), 144 (11), 132 (34), 131 (10), 130 (100, M⁺ - 86, retro Diels-Alder), 128 (12), 115 (11), 109 (14), 102 (56), 100 (53), 93 (13), 73 (13), 65 (58), 63 (15), 53 (16), 51 (25), 50 (14); HRMS calcd for C₇H₅³⁵ClO₃ [(M-CO₂)⁺]: 171.9922; found: 171.9929.

Cycloaddition of 3-Bromo-2(H)-pyran-2-one and Vinylene carbonate

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 3-bromo-2(H)-pyran-2-one **4** (80 mg, 0.46 mmol), vinylene carbonate (0.6 mL, 9.5 mmol, 20 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials.

Proton nuclear magnetic resonance of the crude residue indicated the presence of the *endo* cycloadduct and unreacted starting material (ca 19%). Pure sample of the *endo* cycloadduct was obtained by silica gel chromatography, using 20% v/v ethyl acetate in petroleum ether. Isolated yield of the *endo* cycloadduct was 22 mg, 18%.

***endo* isomer**

m.p. 175 °C; ¹H NMR 6.62 (dd, 1H, J_{1,8} = 1.4 Hz, J_{7,8} = 8.0 Hz, H-8), 6.56 (dd, 1H, J_{1,7} = 5.0 Hz, J_{7,8} = 8.0 Hz, H-7), 5.51 (td, 1H, J_{1,8} = 2.0 Hz, J_{1,7} = J_{1,6} = 4.7 Hz, H-1), 5.20 (dd, 1H, J_{1,6_{exo}} = 4.4 Hz, J_{5,6_{exo}} = 7.8 Hz, H-6), 5.02 (d, 1H, J_{5_{exo},6} = 7.8 Hz, H-5); ¹³C NMR (DMSO-d₆) 164.0 (C-3), 152.7 (CO carbonate), 135.6 (C-8), 130.7 (C-7), 76.8 (C-5), 73.4 (C-6), 71.1 (C-1), 58.4 (C-4); IR 3086, 2962, 2919, 2852, 1846, 1818, 1781, 1375, 1260, 1156, 1101, 1070, 1032, 941, 900, 880, 799, 757, 718 cm⁻¹; m/z 218 [12, M⁺-CO₂(for ⁸¹Br)], 216 [12, M⁺-CO₂(for ⁷⁹Br)], 176 [89, M⁺-86, retro Diels-Alder (for ⁸¹Br)], 174 [100, M⁺-86, retro Diels-Alder (for ⁷⁹Br)], 172 (10), 147 (22), 145 (41), 144 (20), 109 (12), 93 (15), 65 (47), 53 (12); HRMS calcd for C₇H₅⁷⁹BrO₃ [(M-CO₂)⁺]: 215.9422; found: 215.9414.

Cycloaddition of 3-Iodo-2(H)-pyran-2-one and Vinylene carbonate

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 3-Iodo-2(H)-pyran-2-one **11** (61 mg, 0.275 mmol), vinylene carbonate (0.5 mL, 7.9 mmol, 29 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 12 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of cycloadduct and unreacted starting material (ca 8%). Pure sample of the *endo* isomer was obtained by silica gel chromatography, using 25% v/v ethyl acetate in petroleum ether. Isolated yield was 20 mg, 24%.

***endo* isomer**

m.p. 170 °C (dec); ^1H NMR 6.72 (d, 1H, $J_{7,8} = 8.0$ Hz, H-8), 6.39 (dd, 1H, $J_{1,7} = 5.1$ Hz, $J_{7,8} = 8.0$ Hz, H-7), 5.51 (m, 1H, H-1), 5.15 (dd, 1H, $J_{1,6} = 4.3$ Hz, $J_{5,6} = 7.7$ Hz, H-6), 5.08 (dd, 1H, $J_{1,5} = 0.7$ Hz, $J_{5,6} = 7.7$ Hz, H-5); ^{13}C NMR 164.9 (C-3), 152.4 (CO carbonate), 138.6 (C-8), 130.8 (C-7), 78.6 (C-5), 73.4 (C-6), 70.9 (C-1), 34.5 (C-4); IR 2919, 2852, 1841, 1818, 1773, 1375, 1168, 1094, 1080, 1066, 1024, 937, 756, 731 cm^{-1} ; m/z 308 (14, M^+), 264 (31, $\text{M}^+ - \text{CO}_2$), 222 (100, $\text{M}^+ - 86$, retro Diels-Alder), 194 (20), 95 (12), 93 (27), 65 (26), 51 (10); HRMS calcd for $\text{C}_5\text{H}_3\text{IO}_2$ ($\text{M}^+ - 86$, retro Diels-Alder): 221.9172; found: 221.9161.

Cycloaddition of 3-Chloro-2(H)-pyran-2-one and Butyl vinyl ether

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 3-chloro-2(H)-pyran-2-one **10** (52 mg, 0.4 mmol), butyl vinyl ether (0.5 mL, 3.9 mmol, 10 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two cycloadducts. Pure samples of the 5-*endo* and the 5-*exo* cycloadducts were obtained by silica gel chromatography, using 20% v/v ethyl acetate in petroleum ether. Combined isolated yield of cycloadducts was 37 mg, 40%.

4-Chloro-5_{endo}-butoxy-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ^1H NMR 6.54 (dd, 1H, $J_{1,7} = 5.2$ Hz, $J_{7,8} = 8.0$ Hz, H-7), 6.36 (d, 1H, $J_{7,8} = 8.0$ Hz, H-8), 5.22 (ddd, 1H, $J_{1,6\text{endo}} = 1.8$ Hz, $J_{1,6\text{exo}} = 3.6$ Hz, $J_{1,7} = 5.2$ Hz, H-1), 3.84 (dd, 1H, $J_{5,6\text{endo}} = 1.6$ Hz, $J_{5,6\text{exo}} = 7.8$ Hz, H-5), 3.72 -3.41 (m, 2H, OCH_2),

2.69 (ddd, 1H, $J_{1,6_{\text{exo}}} = 3.8$ Hz, $J_{5,6_{\text{exo}}} = 7.8$ Hz, $J_{6_{\text{exo}},6_{\text{endo}}} = 13.9$ Hz, H-6_{exo}), 1.79 (dt, 1H, $J_{1,6_{\text{endo}}}$, $J_{5,6_{\text{endo}}} = 1.6$ Hz, $J_{6_{\text{exo}},6_{\text{endo}}} = 13.9$ Hz, H-6_{endo}), 1.54 (m, 2H, OCH₂CH₂), 1.37 (m, 2H, CH₂CH₃), 0.91 (t, 3H, $J = 7.3$ Hz, CH₃); ¹³C NMR 168.6 (C-3), 135.1 (C-7), 130.5 (C-8), 76.3 (C-5), 73.1 (C-1), 72.3 (OCH₂), 60.0 (C-4), 37.2 (C-6), 32.2 (OCH₂CH₂), 19.5 (CH₂CH₃), 14.2 (CH₃); IR 2960, 2926, 2852, 1770, 1464, 1361, 1260, 1101, 1042, 894, 801, 713 cm⁻¹; m/z 233 (14), 232 (8), 231 (32, M⁺), 195 (10), 176 (7), 175 (13), 159(15), 158 (9, M⁺-BuO), 157 (11), 150 (12), 133 (15), 132 (9), 131 (23), 123 (52), 115 (14, M⁺-BuO-CO₂), 114 (14), 113 (21), 112 (18), 111 (11), 102 (13), 101 (21), 100 (25), 95 (40), 94 (10), 85 (31), 79 (16), 78 (31), 77 (100), 75 (12), 73 (13, BuO), 67 (13), 66 (16), 65 (33), 63 (14), 57 (26), 56 (17), 55 (13), 53 (11), 52 (14), 51 (16), 50 (14); HRMS calcd for C₁₁H₁₅ClO₃Na: 253.06074; found: 253.06183.

4-Chloro-5_{exo}-butoxy-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.52 (dd, 1H, $J_{1,7} = 4.9$ Hz, $J_{7,8} = 8.0$ Hz, H-7), 6.37 (dd, 1H, $J_{1,8} = 1.9$ Hz, $J_{7,8} = 8.0$ Hz, H-8), 5.22 (m, 1H, H-1), 3.82 (dd, 1H, $J_{5,6_{\text{endo}}} = 3.0$ Hz, $J_{5,6_{\text{exo}}} = 8.3$ Hz, H-5), 5.65 - 3.55 (m, 2H, OCH₂), 2.24 - 2.14 (m, 2H, H-6), 1.70 - 1.42 (m, 2H, OCH₂CH₂), 1.40 - 1.30 (m, 2H, CH₂CH₃), 0.90 (t, 3H, $J = 7.3$ Hz, CH₃); ¹³C NMR 168.6 (C-3), 135.53 (C-7), 133.4 (C-8), 78.1 (C-5), 73.8 (C-1), 72.0 (OCH₂), 62.0 (C-4), 35.8 (C-6), 32.1 (OCH₂CH₂), 19.6 (CH₂CH₃), 14.2 (CH₃); IR 2959, 2928, 2872, 1780, 1465, 1360, 1248, 1104, 1050, 954, 895, 706 cm⁻¹; m/z 233 (10), 232 (8), 231 (22, M⁺), 204 (10), 196 (9), 195 (14, M⁺-Cl), 177 (15), 176 (12), 175 (16), 174 (14), 160 (21), 159(12), 158 (22, M⁺ - BuO), 157 (9), 150 (24), 147 (14), 139(11), 133 (22), 132 (16), 131 (43), 130 (24), 123 (37), 116 (25), 115 (15), 114 (55), 113 (19), 112 (12), 111 (9), 102 (12), 101 (14), 100 (73), 96 (13), 95 (100), 94 (10), 86 (11), 85 (81), 79 (23), 78 (9), 77 (22), 67 (19), 66 (12), 65 (11), 57 (41), 56 (53), 55 (8); HRMS calcd for C₁₁H₁₅ClO₃Na: 253.06019; found: 253.06063.

Cycloaddition of 3-Bromo-2(H)-pyran-2-one and (2-chloroethyl) vinyl ether

A sealed pressure tube (purchased from Aldrich Chemical Co Cat No Z18, 109-9) was charged with 3-bromo-2(H)-pyran-2-one **5** (100 mg, 0.57 mmol), 2-chloroethyl vinyl ether (0.6 mL, 5.9 mmol, 10 equiv), a few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two cycloadducts. Pure samples of the *5-endo* and the *5-exo* cycloadducts were obtained by silica gel chromatography using 10-40% v/v ethyl acetate in petrol ether. Combined isolated yield of cycloadducts was 104 mg, 65%.

4-Bromo-5_{endo}-(2-chloroethoxy)-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.50 (dd, 1H, J_{1,7} = 5.2 Hz, J_{7,8} = 8.0 Hz, H-7), 6.45(d, 1H, J_{7,8} = 8.0 Hz, H-8), 5.24 (ddd, 1H, J_{1,6endo} = 1.8 Hz, J_{1,6exo} = 3.7 Hz, J_{1,7} = 5.2 Hz, H-1), 4.08 (dt, 1H, J = 5.0 Hz, 11.2 Hz, OCH₂HCH₂Cl), 3.98 (dm, 1H, J_{5,6exo} = 7.8 Hz, H-5), 3.81 (ddd, 1H, J = 5.0 Hz, 6.4 Hz, 11.2 Hz, OCH₂HCH₂Cl), 3.60 (m, 2H, OCH₂CH₂Cl), 2.74 (ddd, 1H, J_{1,6exo} = 3.7 Hz, J_{5,6exo} = 7.8 Hz, J_{6exo,6endo} = 14.0 Hz, H-6_{exo}), 1.82 (dd, 1H, J_{1,6endo} = 1.8 Hz, J_{6exo,6endo} = 14.0 Hz, H-6_{endo}); ¹³C NMR 166.5 (C-3), 134.4 (C-7), 129.6 (C-8), 76.6 (C-1), 71.8 (C-5), 71.4 (OCH₂CH₂Cl), 63.2 (C-4), 42.0 (OCH₂CH₂Cl), 36.1 (C-6); IR 2960, 2926, 2855, 1765, 1690, 1653, 1461, 1431, 1362, 1339, 1300, 1260, 1235, 1173, 1120, 1079, 1038, 986, 904, 850, 738, 710, 693, 666, 613, 594 cm⁻¹; m/z 280 (12), 267 (18), 265 (20), 239 (19), 225 (20), 221 (15), 215 (19), 211 (16), 209 (17), 207 (16), 199 (16), 197 (22), 187 (18), 174 (14), 173 (15), 172 (15), 171 (25), 161 (18), 137 (15), 135 (18), 133 (33), 127 (17), 116 (15), 109 (41), 107 [100, (M⁺-175, retro Diels-Alder)], 96 (15), 82 (15), 81 (15), 65 (18), 63 (94, M⁺-106-Br); HRMS calcd for C₉H₁₀⁸¹Br³⁵ClO₃Na: 304.93736; found: 304.93801.

4-Bromo-5_{exo}-(2-chloroethoxy)-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.53 (dd, 1H, J_{1,8} = 2.2 Hz, J_{7,8} = 8.0 Hz, H-8), 6.49 (dd, 1H, J_{1,7} = 5.0 Hz, J_{7,8} = 8.0 Hz, H-7), 5.24 (ddd, 1H, J_{1,6endo} = 1.8 Hz, J_{1,6exo} = 3.2 Hz, J_{1,7} = 5.0 Hz, H-1), 4.06 and 3.83 (m, 2H, OCH₂CH₂Cl), 4.01 (dd, 1H, J_{5,6exo} = 5.0 Hz, J_{5,6endo} = 7.0 Hz, H-5), 3.62 (m, 2H, OCH₂CH₂Cl), 2.30 (m, 2H, H-6); ¹³C NMR 165.4 (C-3), 134.7 (C-8), 132.5 (C-7), 78.7 (C-1), 72.6 (C-5), 71.4 (OCH₂CH₂Cl), 62.9 (C-4), 41.8 (OCH₂CH₂Cl), 34.8 (C-6); IR 2926, 2855, 1776, 1461, 1360, 1299, 1266, 1197, 1115, 1039, 956, 896, 803, 738, 704, 668, 612 cm⁻¹; m/z 283 (3), 281 (1), 203 (4), 201 (7), 176 [6, (M⁺ for ⁸¹Br - 106, retro Diels-Alder)], 174 [5, (M⁺ for ⁷⁹Br - 106, retro Diels-Alder)], 160 (9), 159 (33), 158 (20), 157 (100, M⁺-CO₂-Br), 156 (8), 147 (38), 145 (41), 123 (20), 121 (33), 108 (23), 107 (11), 106 [67 (M⁺-176, retro Diels-Alder)], 95 (43), 94 (12), 93 (10), 79 (14), 78 (50), 77 (78), 67 (19), 66 (29), 65 (50), 63 (65), 62 (12), 52 (14), 51 (30), 50 (15); HRMS calcd for C₉H₁₀⁸¹Br³⁵ClO₃Na: 304.93736; found: 304.93725.

Cycloaddition of 3-Iodo-2(H)-pyran-2-one and Butyl vinyl ether

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 3-iodo-2(H)-pyran-2-one **11** (50 mg, 0.225 mmol), butyl vinyl ether (0.5 mL, 3.9 mmol, 17 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of cycloadducts. Pure samples of the 5-*endo* and the 5-*exo* cycloadducts were obtained by silica gel chromatography, using 20% v/v ethyl acetate in petroleum ether. Combined isolated yield of cycloadducts was 52 mg, 78%.

4-Iodo-5_{endo}-butoxy-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.57 (dm, 1H, J_{7,8} = 7.8 Hz, H-8), 6.28 (dd, 1H, J_{1,7} = 5.1 Hz, J_{7,8} = 7.8 Hz, H-7), 5.25 (ddd, 1H, J_{1,6endo} = 1.7 Hz, J_{1,6exo} = 3.5 Hz, J_{1,7}

= 5.1 Hz, H-1), 3.85 (dm, 1H, $J_{5,6\text{exo}} = 7.4$ Hz, H-5), 3.56 (m, 2H, OCH_2), 2.59 (ddd, 1H, $J_{1,6\text{exo}} = 3.5$ Hz, $J_{5,6\text{exo}} = 7.5$ Hz, $J_{6\text{exo},6\text{endo}} = 13.6$ Hz, H-6_{exo}), 1.84 (dm, 1H, $J_{6\text{exo},6\text{endo}} = 13.6$ Hz, H-6_{endo}), 1.56 (m, 2H, OCH_2CH_2), 1.40 (m, 2H, CH_2CH_3), 0.93 (t, 3H, $J = 7.3$ Hz, CH_3); ^{13}C NMR 168.6 (C-3), 138.8 (C-8), 130.9 (C-7), 77.9 (C-1), 73.3 (C-5), 71.4 (OCH_2), 45.2 (C-4), 36.4 (C-6), 32.1 (OCH_2CH_2), 19.7 (CH_2CH_3), 14.3 (CH_3); IR 2957, 2926, 2855, 1760, 1464, 1360, 1336, 1296, 1233, 1169, 1104, 1070, 1033, 970, 894, 705, 610, 592 cm^{-1} ; m/z 323 (4, MH^+), 322 (3, M^+), 223 [34, ($\text{MH}^+ - 100$, retro Diels-Alder)], 222 (31), 206 (10), 196 (10), 195 (51, $\text{M}^+ - \text{I}$), 194 (11), 139 [14, ($\text{MH}^+ - \text{I-Bu}$)], 123 (18), 101 (16), 100 (59), 95 (38), 85 (100), 67 (11), 57 (22), 56 (49); HRMS calcd for $\text{C}_{11}\text{H}_{15}\text{IO}_3\text{Na}$: 344.99655; found: 344.99751.

4-Iodo-5_{exo}-butoxy-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ^1H NMR 6.74 (dd, 1H, $J_{1,8} = 1.9$ Hz, $J_{7,8} = 7.9$ Hz, H-8), 6.30 (dd, 1H, $J_{1,7} = 4.9$ Hz, $J_{7,8} = 7.9$ Hz, H-7), 5.25 (m, 1H, H-1), 3.82 (dd, 1H, $J_{5,6\text{exo}} = 3.3$ Hz, $J_{5,6\text{endo}} = 8.4$ Hz, H-5), 3.58 (ddd, 1H, $J = 2.8, 9.0,$ and 15.3 Hz, OCHHPr), 3.48 (ddd, 1H, $J = 2.8, 9.0,$ and 15.3 Hz, OCHHPr), 2.25 (dt, 1H, $J_{1,6\text{exo}} = 3.3$ Hz, $J_{5,6\text{exo}} = 3.3$ Hz, $J_{6\text{exo},6\text{endo}} = 13.3$ Hz, H-6_{exo}), 2.09 (ddd, 1H, $J_{1,6\text{endo}} = 1.4$ Hz, $J_{5,6\text{endo}} = 8.4$ Hz, $J_{6\text{exo},6\text{endo}} = 13.3$ Hz, H-6_{endo}), 1.58 (m, 2H, OCH_2CH_2), 1.41 (m, 2H, CH_2CH_3), 0.91 (t, 3H, $J = 7.3$ Hz, CH_3); ^{13}C NMR 168.6 (C-3), 139.0 (C-8), 133.8 (C-7), 79.7 (C-1), 74.3 (C-5), 71.1 (OCH_2), 44.7 (C-4), 34.8 (C-6), 32.0 (OCH_2CH_2), 19.8 [$\text{O}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$], 14.2 (CH_2CH_3); IR 2962, 2930, 2872, 1770, 1608, 1464, 1359, 1244, 1102, 1024, 962, 892, 804, 736, 703 cm^{-1} ; m/z 323 (8, MH^+), 322 (2, M^+), 251 (9), 223 [57, ($\text{MH}^+ - 100$, retro Diels-Alder)], 222 (58), 206 (51), 196 (15), 195 (100, $\text{M}^+ - \text{I}$), 194 (19), 139 [23, ($\text{MH}^+ - \text{I-Bu}$)], 123 (55), 101 (14), 100 (74), 95 (98), 85 (76), 79 (12), 78 (11), 67 (32), 57 (30), 56 (55); HRMS calcd for $\text{C}_{11}\text{H}_{15}\text{IO}_3\text{Na}$: 344.99655; found: 344.99707.

Cycloaddition of 3-Chloro-2(H)-pyran-2-one and 4-Bromostyrene

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 3-Chloro-2(H)-pyran-2-one **10** (51 mg, 0.39 mmol), 4-bromostyrene (0.5 mL, 3.8 mmol, 10 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of cycloadducts. Silica gel chromatography, using 20% v/v ethyl acetate in petroleum ether, afforded a pure sample of the 5-*endo* and 5-*exo* cycloadducts. Combined isolated yield of cycloadducts was 93 mg, 76%.

4-Chloro-5_{endo}-(4-bromophenyl)-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 131 °C; ¹H NMR 7.43 (d, 2H, J = 8.4 Hz, aromatic H), 7.05 (d, J = 8.4 Hz, aromatic H), 6.75 (dd, 1H, J_{1,7} = 5.2 Hz, J_{7,8} = 8.0 Hz, H-7), 6.29 (d, 1H, J_{7,8} = 8.0 Hz, H-8), 5.39 (m, 1H, H-1), 3.31 (dd, 1H, J_{5,6endo} = 4.4 Hz, J_{5,6exo} = 9.6 Hz, H-5), 2.95 (ddd, 1H, J_{1,6exo} = 4.2 Hz, J_{5,6exo} = 9.6 Hz, J_{6exo,6endo} = 13.9 Hz, H-6_{exo}), 2.05 (ddd, 1H, J_{1,6endo} = 1.3 Hz, J_{5,6endo} = 4.4 Hz, J_{6exo,6endo} = 13.9 Hz, H-6_{endo}); ¹³C NMR 168.1 (C-3), 136.5 (aromatic C-1'), 134.0 (aromatic C-2' and C-6'), 131.1 (aromatic C-3' and C-5'), 130.4 (C-7), 129.9 (C-8), 121.2 (aromatic C-4'), 72.5 (C-1), 69.0 (C-4), 42.7 (C-5), 35.7 (C-6); IR 2924, 2852, 1766, 1592, 1490, 1411, 1362, 1276, 1168, 1121, 1075, 1043, 1010, 999, 940, 863, 824, 728, 704 cm⁻¹; m/z 314 (10, M⁺), 270 (24, M⁺-CO₂), 268 (17), 235 [43, (M⁺ for ⁸¹Br-CO₂-Cl)], 234 (12), 233 (45), 185 [33, (M⁺ for ⁸¹Br-130, retro Diels-Alder)], 183 (34), 171 (12), 169(12), 155 (29), 154 (100), 153 (76), 151 (19), 103 (57), 77 (9); HRMS calcd for C₁₃H₁₀⁸¹Br³⁷ClO₂Na: 334.94510; found: 334.94575.

4-Chloro-5_{exo}-(4-bromophenyl)-3-oxo-2-oxabicyclo[2.2.2]oct-7-en-3-one ¹H NMR 7.45 (d, 2H, J = 8.2 Hz, aromatic H), 7.07 (d, 2H, J = 8.2 Hz, aromatic H), 6.68 (dd, 1H, J_{1,7} = 5.2 Hz, J_{7,8} = 7.8 Hz, H-7), 6.43 (d, 1H, J_{7,8} = 7.8 Hz, H-8), 5.38 (m, 1H, H-1), 3.25 (dd, 1H, J_{5,6exo} = 6.2 Hz, J_{5,6endo} = 10.1

Hz, H-5), 2.48 (m, 1H, H-6_{exo}), 2.45 (m, 1H, H-6_{endo}); ¹³C NMR 168.2, 138.4 (C-8), 136.6 (aromatic C-1'), 132.0 (C-7), 131.8 (aromatic C-2' and C-6'), 130.5 (aromatic C-3' and C-5'), 122.2 (aromatic C-4'), 73.6 (C-1), 70.4 (C-4), 47.0 (C-5), 36.2 (C-6); IR 3085, 2925, 2849, 1764, 1486, 1410, 1359, 1255, 1146, 1123, 1109, 1076, 1043, 1009, 948, 873, 826, 802, 774, 717, 698 cm⁻¹; m/z 314 (5, M⁺ for ⁸¹Br), 312 (4, M⁺ for ⁷⁹Br), 270 (4, M⁺-CO₂), 268 (3, M⁺-CO₂), 235 (4), 234 (3), 233 (4), 185 (13), 184 [95, (M⁺ for ⁸¹Br-130, retro Diels-Alder)], 183 (10), 182 [100, (M⁺ for ⁷⁹Br-130, retro Diels-Alder)], 154 (11), 127 (12), 125 (14), 113 (14), 112 (10), 111 (20), 99 (16), 98 (10), 97 (23), 85 (31), 84 (13), 83 (18), 71 (37), 70 (12), 69(10), 57 (37); HRMS calcd for C₁₃H₁₁⁸¹Br³⁵ClO₂ (MH⁺): 314.96050; found: 314.96153.

Cycloaddition of 3-Bromo-2(H)-pyran-2-one and 4-Bromostyrene

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 3-bromo-2(H)-pyran-2-one **4** (110 mg, 0.63 mmol), 4-bromostyrene (0.6 mL, 4.6 mmol, 7 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of cycloadducts. Silica gel chromatography, using 20% v/v ethyl acetate in petroleum ether, afforded a pure sample of the 5-*endo* cycloadduct and a mixture of the 5-*endo* and 5-*exo* cycloadducts. Combined isolated yield of cycloadducts was 116 mg, 52%.

4-Bromo-5_{endo}-(4-bromophenyl)-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 146 °C; ¹H NMR 7.44 (d, 2H, J = 8.5 Hz, aromatic H), 7.06 (d, J = 8.5 Hz, aromatic H), 6.68 (dd, 1H, J_{1,7} = 5.2 Hz, J_{7,8} = 8.0 Hz, H-7), 6.43 (d, 1H, J_{7,8} = 8.0 Hz, H-8), 5.40 (m, 1H, H-1), 3.36 (dd, 1H, J_{5,6endo} = 4.4 Hz, J_{5,6exo} =

9.6 Hz, H-5), 2.95 (ddd, 1H, $J_{1,6\text{exo}} = 4.2$ Hz, $J_{5,6\text{exo}} = 9.6$ Hz, $J_{6\text{exo},6\text{endo}} = 13.9$ Hz, H-6_{exo}), 2.06 (ddd, 1H, $J_{1,6\text{endo}} = 1.2$ Hz, $J_{5,6\text{endo}} = 4.4$ Hz, $J_{6\text{exo},6\text{endo}} = 13.9$ Hz, H-6_{endo}); ¹³C NMR 169.0 (C-3), 139.0 (aromatic C-1'), 136.4 (aromatic C-2' and C-6'), 132.9 (aromatic C-3' and C-5'), 131.8 (C-7), 131.2 (C-8), 122.6 (aromatic C-4'), 74.2 (C-1), 64.0 (C-4), 44.7 (C-5), 37.5 (C-6); IR 2945, 1763, 1489, 1362, 1164, 1121, 1075, 1036, 1010, 998, 861, 822, 726, 704, 530, 455 cm⁻¹; m/z 360 (2, M⁺ for ⁸¹Br), 358 (3, M⁺), 356 (2, M⁺ for ⁷⁹Br), 316 (9), 314 (18, M⁺-CO₂), 312 (10), 235 (8, M⁺ for ⁸¹Br-CO₂-Br), 233 (8), 185 (11), 184 [100, (M⁺ for ⁸¹Br - 176, retro Diels-Alder)], 183(11), 182 [100, (M⁺ for ⁷⁹Br - 174, retro Diels-Alder)], 155 (9), 154 (64), 153 (21), 151(13), 103 (8), 77(18), 76 (19), 44(7); HRMS calcd for C₁₃H₁₀⁸¹Br₂O₂Na: 382.88988; found: 382.89055; Anal calcd for C₁₃H₁₀Br₂O₂: C, 43.61, H, 2.82; found: C, 43.81, H, 2.98.

4-Bromo-5_{exo}-(4-bromophenyl)-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 7.45 (d, 2H, J = 8.3 Hz, aromatic H), 7.06 (d, J = 8.3 Hz, aromatic H), 6.77 (d, 1H, $J_{1,8} = 1.9$ Hz, $J_{7,8} = 7.9$ Hz, H-8), 6.54 (dd, 1H, $J_{1,7} = 5.0$ Hz, $J_{7,8} = 7.9$ Hz, H-7), 5.39 (m, 1H, H-1), 3.30 (dd, 1H, $J_{5,6\text{exo}} = 5.8$ Hz, $J_{5,6\text{endo}} = 10.4$ Hz, H-5), 2.50 (ddd, 1H, $J_{1,6\text{exo}} = 3.8$ Hz, $J_{5,6\text{exo}} = 5.8$ Hz, $J_{6\text{exo},6\text{endo}} = 13.9$ Hz, H-6_{exo}), 2.43 (ddd, 1H, $J_{1,6\text{endo}} = 1.7$ Hz, $J_{5,6\text{endo}} = 10.4$ Hz, $J_{6\text{exo},6\text{endo}} = 13.9$ Hz, H-6_{endo}); ¹³C NMR 169.0 (C-3), 139.9 (aromatic C-2' and C-6'), 138.0 (aromatic C-1'), 132.6 (aromatic C-3' and C-5'), 132.2 (C-8), 130.8 (C-7), 122.5 (aromatic C-4'), 74.3 (C-1), 63.1 (C-4), 48.1 (C-5), 36.9 (C-6).

Cycloaddition of 3-Iodo-2(H)-pyran-2-one and 4-Bromostyrene

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 3-Iodo-2(H)-pyran-2-one **8** (80 mg, 0.36 mmol), 4-bromostyrene (0.5 ml, 3.8 mmol, 10 equiv), few crystals of 2,6-di-*tert*-butyl 4-methyl phenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3

days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two isomers of cycloadducts. Silica gel chromatography, using 25% v/v ethyl acetate in petroleum ether, afforded a pure sample of the 5-*endo* cycloadduct and a mixture of the 5-*endo* and 5-*exo* cycloadducts. Combined isolated yield of cycloadducts was 136 mg, 93%.

4-Iodo-5-*endo*-(4-bromophenyl)-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 145-146 °C; ^1H NMR 7.45 (d, 2H, $J = 8.5$ Hz, aromatic H), 7.06 (d, 2H, $J = 8.5$ Hz, aromatic H), 6.61 (d, 1H, $J_{7,8} = 8.0$ Hz, H-8), 6.50 (dd, 1H, $J_{1,7} = 5.1$ Hz, $J_{7,8} = 8.0$ Hz, H-7), 5.40 (m, 1H, H-1), 3.35 (dd, 1H, $J_{5,6\text{endo}} = 4.5$ Hz, $J_{5,6\text{exo}} = 9.5$ Hz, H-5), 2.91 (ddd, 1H, $J_{1,6\text{exo}} = 4.2$ Hz, $J_{5,6\text{exo}} = 9.5$ Hz, $J_{6\text{endo},6\text{exo}} = 13.7$ Hz, H-6_{exo}), 2.07 (ddd, 1H, $J_{1,6\text{endo}} = 1.1$ Hz, $J_{5,6\text{endo}} = 4.5$ Hz, $J_{6\text{endo},6\text{exo}} = 13.7$ Hz, H-6_{endo}); ^{13}C NMR 169.4 (C-3), 140.9 (aromatic C-1'), 138.9 (aromatic C-2' and C-6'), 133.5 (aromatic C-3' and C-5'), 131.8 (C-8), 131.1 (C-7), 122.5 (aromatic C-4'), 74.4 (C-1), 46.5 (C-4), 46.5 (C-5), 37.2 (C-6); IR 3002, 2930, 2846, 1751, 1661, 1589, 1488, 1443, 1407, 1362, 1340, 1270, 1180, 1155, 1121, 1074, 1054, 1030, 1010, 993, 962, 937, 876, 858, 831, 814, 744, 713 cm^{-1} ; m/z 406 (6, M^+ for ^{81}Br), 404 (6, M^+ for ^{79}Br), 362 (7), 222 (9, $\text{M}^+ - 183$, retro Diels-Alder), 194 (9), 184 (95, M^+ for $^{81}\text{Br} - 222$, retro Diels-Alder), 182 (100, M^+ for $^{79}\text{Br} - 222$, retro Diels-Alder), 154 (28, $\text{M}^+ - \text{CO}_2, -\text{I}, -\text{Br}$), 153 (17), 152 (13), 127 (8), 103 (11); HRMS calcd for $\text{C}_{13}\text{H}_{10}^{79}\text{BrIO}_2\text{Na}$: 426.88011; found: 426.88079.

4-Iodo-5-*exo*-(4-bromophenyl)-2-oxabicyclo[2.2.2]oct-7-en-3-one ^1H NMR 7.46 (d, 2H, 8.3 Hz, aromatic H), 7.06 (d, $J = 8.3$ Hz, aromatic H), 7.01 (dd, 1H, $J_{1,8} = 2.0$ Hz, $J_{7,8} = 8.0$ Hz, H-8), 6.37 (dd, 1H, $J_{1,7} = 5.0$ Hz, $J_{7,8} = 8.0$ Hz, H-7), 5.40 (m, 1H, H-1), 3.30 (dd, 1H, $J_{5,6\text{exo}} = 5.6$ Hz, $J_{5,6\text{endo}} = 10.8$ Hz, H-5), 2.53 (ddd, 1H, $J_{1,6\text{exo}} = 3.9$ Hz, $J_{5,6\text{exo}} = 5.6$ Hz, $J_{6\text{exo},6\text{endo}} = 13.8$ Hz, H-6_{exo}), 2.36 (ddd, 1H, $J_{1,6\text{endo}} = 1.5$ Hz, $J_{5,6\text{endo}} = 10.8$ Hz, $J_{6\text{exo},6\text{endo}} = 13.8$ Hz, H-6_{endo}); ^{13}C NMR 169.0 (C-3), 142.9

(aromatic C-2' and C-6'), 139.8 (aromatic C-1'), 132.8 (aromatic C-3' and C-5'), 132.2 (C-8), 131.0 (C-7), 122.5 (aromatic C-4'), 74.5 (C-1), 49.8 (C-5), 46.4 (C-4), 36.6 (C-6).

Cycloaddition of 5-Chloro-2(H)-pyran-2-one and Methyl Acrylate

A sealed pressure tube (purchased from Aldrich Chemical Co Cat No Z18, 109-9) was charged with 5-chloro-2(H)-pyran-2-one **12** (30 mg, 0.23 mmol), methyl acrylate (0.4 mL, 4.5 mmol, 19.5 equiv), a few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and immersed in an oil bath maintained at 90 °C. After 4 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of 3 isomers of cycloadducts. Silica gel chromatography using 20% v/v ethyl acetate in petrol ether afforded pure samples of the 5-*endo* and 5-*exo* cycloadducts as well a sample of the 6-*endo* product contaminated with traces of the 5-*endo* and 5-*exo* cycloadducts. Combined isolated yield of cycloadducts was 41mg, 83 %.

Methyl 7-chloro-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5_{endo}-carboxylate ¹H NMR 6.32 (dd, 1H, J_{1,8} = 2.5 Hz, J_{4,8} = 6.6 Hz, H-8), 5.11 (m, 1H, H-1), 3.94 (dd, 1H, J_{4,5} = 2.7 Hz, J_{4,8} = 6.6 Hz, H-4), 3.74 (s, 3H, CO₂CH₃), 3.09 (dm, 1H, J_{5,6_{exo}} = 9.6 Hz, H-5), 2.54 (ddd, 1H, J_{1,6_{exo}} = 3.9 Hz, J_{5,6_{exo}} = 9.6 Hz, J_{6_{exo},6_{endo}} = 14.0 Hz, H-6_{exo}), 2.29 (ddd, 1H, J_{1,6_{endo}} = 1.5 Hz, J_{5,6_{endo}} = 4.0 Hz, J_{6_{exo},6_{endo}} = 14.0 Hz, H-6_{endo}); ¹³C NMR 171.7 (C=O), 171.0 (C-3), 135.0 (C-7), 124.6 (C-8), 79.5 (C-1), 53.2 (CO₂CH₃), 44.4 (C-4), 37.5 (C-5), 30.2 (C-6); IR 2922, 2852, 1767, 1738, 1621, 1436, 1358, 1214, 1158, 1024, 997, 951, 900, 809, 782, 765 cm⁻¹; m/z 218 (4, M⁺ for ³⁷Cl), 217 (7), 216 (10, M⁺ for ³⁵Cl), 185 [26, (M⁺-OMe)], 172 [25, (M⁺-CO₂)], 171 (10), 141 (11), 137 (12), 130 [18, (M⁺-86, retro Diels-Alder)], 115 (42), 114 (28), 113 [100, (M⁺-CO₂-CO₂Me)], 112 (59), 102 (15), 78 (20), 77 (100), 65 (10), 60

(11), 55 (49), 50 (17), 39 (14); HRMS calcd for $C_9H_9^{35}ClO_4Na$: 239.00816; found: 239.00803; Anal. calcd for $C_9H_9ClO_4$: C, 49.90, H, 4.19; found: C, 50.11, H, 4.05.

Methyl 7-chloro-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-6_{endo}-carboxylate 1H NMR 6.47 (dd, 1H, $J_{1,8} = 2.7$ Hz, $J_{4,8} = 6.8$ Hz, H-8), 5.36 (dd, 1H, $J_{1,8} = 2.7$ Hz, $J_{1,6} = 3.9$ Hz, H-1), 3.76 (s, 3H, CO_2CH_3), 3.58 (dt, 1H, $J_{4,5endo} = 2.9$ Hz, $J_{4,8} = 6.8$ Hz, H-4), 3.43 (ddd, 1H, $J_{1,6} = 3.9$ Hz, $J_{5endo,6} = 5.3$ Hz, $J_{5exo,6} = 9.4$ Hz, H-6), 2.22 (ddd, 1H, $J_{4,5exo} = 3.0$ Hz, $J_{5exo,6} = 9.4$ Hz, $J_{5exo,5endo} = 13.2$ Hz, H-5_{exo}), 2.12 (ddd, 1H, $J_{4,5endo} = 2.8$ Hz, $J_{5endo,6} = 5.3$ Hz, $J_{5exo,5endo} = 13.2$ Hz, H-5_{endo}); ^{13}C NMR 171.6 (CO_2CH_3), 171.0 (C-3), 132.5 (C-7), 127.9 (C-8), 79.7 (C-1), 53.0 (CO_2CH_3), 43.6 (C-4), 41.6 (C-6), 24.2 (C-5); IR 3077, 2956, 2923, 2852, 1770, 1741, 1621, 1438, 1360, 1215, 1025, 998, 953, 901, 785, 770 cm^{-1} .

Methyl 7-chloro-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5_{exo}-carboxylate 1H NMR 6.43 (dd, 1H, $J_{1,8} = 2.6$ Hz, $J_{4,8} = 6.9$ Hz, H-8), 5.10 (m, 1H, H-1), 3.77 (dd, $J_{4,5} = 2.2$ Hz, $J_{4,8} = 6.9$ Hz, H-4), 3.76 (s, 3H, CO_2CH_3), 2.83 (ddd, 1H, $J_{4,5} = 2.2$ Hz, $J_{5,6exo} = 5.3$ Hz, $J_{5,6endo} = 10.8$ Hz, H-5), 2.55 (ddd, 1H, $J_{1,6exo} = 4.0$ Hz, $J_{5,6exo} = 5.3$ Hz, $J_{6endo,6exo} = 13.9$ Hz, H-6_{exo}), 2.18 (ddd, 1H, $J_{1,6endo} = 1.7$ Hz, $J_{5,6endo} = 10.8$ Hz, $J_{6endo,6exo} = 13.9$ Hz, H-6_{endo}); ^{13}C NMR 170.8 (CO_2CH_3), 168.4 (C-3), 134.5 (C-7), 124.5 (C-8), 77.8 (C-1), 51.9 (CO_2CH_3), 43.4 (C-4), 38.3 (C-5), 28.3 (C-6); IR 2923, 2852, 1773, 1738, 1438, 1354, 1265, 1208, 1134, 1013, 917, 802, 737 cm^{-1} ; m/z 218 (4, M^+ for ^{37}Cl), 217 (16), 216 (6, M^+ for ^{35}Cl), 187 (19), 185 [21, (M^+ -OMe)], 172 [23, (M^+ -CO₂)], 171 (13), 157 (11), 141 (14), 137 (13), 130 [21, (M^+ -86, retro Diels-Alder)], 127 (11), 115 (47), 114 (30), 113 [100, (M^+ -CO₂-CO₂Me)], 112 (60), 102 (15), 78 (18), 77 (100), 65 (11), 60 (14), 59 (22), 57 (12), 55 (43), 43 (10), 39 (14); HRMS calcd for $C_9H_9^{35}ClO_4Na$: 239.00816; found: 239.00792.

Cycloaddition of 5-Bromo-2(H)-pyran-2-one and Methyl Acrylate

A sealed pressure tube (purchased from Aldrich Chemical Co Cat No Z18, 109-9) was charged with 5-bromo-2(H)-pyran-2-one **5** (66 mg, 0.38 mmol), methyl acrylate (0.6 mL, 6.7 mmol, 18 equiv), a few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of 3 isomers of cycloadducts. Silica gel chromatography using 30% v/v ethyl acetate in petrol ether afforded pure samples of the 5-*endo* and 5-*exo* cycloadducts as well a sample of the 6-*endo* product contaminated with traces of the 5-*endo* and 5-*exo* cycloadducts. Combined isolated yield of cycloadducts was 93 mg, 94%.

Methyl 7-bromo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5_{endo}-carboxylate ¹H NMR 6.53 (dd, 1H, J_{1,8} = 2.4 Hz, J_{4,8} = 6.5 Hz, H-8), 5.16 (m, 1H, H-1), 3.91 (dd, 1H, J_{4,5} = 2.7 Hz, J_{4,8} = 6.5 Hz, H-4), 3.72 (s, 3H, CO₂CH₃), 3.05 (dm, 1H, J_{5,6_{exo}} = 9.4 Hz, H-5), 2.50 (ddd, 1H, J_{1,6_{exo}} = 3.9 Hz, J_{5,6_{exo}} = 9.8 Hz, J_{6_{exo},6_{endo}} = 14.0 Hz, H-6_{exo}), 2.26 (ddd, 1H, J_{1,6_{endo}} = 1.4 Hz, J_{5,6_{endo}} = 4.0 Hz, J_{6_{exo},6_{endo}} = 14.0 Hz, H-6_{endo}); ¹³C NMR 171.7 (C-3), 170.8 (CO₂CH₃), 129.3 (C-8), 122.0 (C-7), 80.9 (C-1), 53.2 (CO₂CH₃), 45.5 (C-4), 37.2 (C-5), 30.1 (C-6); IR 3005, 2954, 2850, 1766, 1734, 1615, 1436, 1359, 1275, 1235, 1214, 1158, 1073, 1042, 1014, 995, 951, 902, 808, 783, 767, 736, 642, 521 cm⁻¹; m/z 262 (14, M⁺ for ⁸¹Br), 260 (14, M⁺ for ⁷⁹Br), 231 [17, (M⁺ for ⁸¹Br-OMe)], 229 [18, (M⁺ for ⁷⁹Br-OMe)], 218 [16, (M⁺ for ⁸¹Br-CO₂)], 216 [16, (M⁺ for ⁷⁹Br-CO₂)], 187 (6), 185 (6), 176 [14, (M⁺ for ⁸¹Br-86, retro Diels-Alder)], 174 [14, (M⁺ for ⁷⁹Br-86, retro Diels-Alder)], 159 [90, (M⁺ for ⁸¹Br-CO₂-CO₂Me)], 158 (40), 157 [93, (M⁺ for ⁷⁹Br-CO₂-CO₂Me)], 156 (34), 147 (11), 145 (11), 93 (37), 78 (95), 77 (100), 65 (11),

60 (10), 59 (19), 55 (60); HRMS calcd for $C_9H_9^{79}BrO_4Na$: 282.95825; found: 282.95796; Anal. calcd for $C_9H_9BrO_4$: C, 41.41, H, 3.47; found: C, 41.61, H, 3.34.

Methyl 7-bromo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-6_{endo}-carboxylate 1H NMR 6.68 (dd, 1H, $J_{1,8} = 2.6$ Hz, $J_{4,8} = 6.8$ Hz, H-8), 5.42 (dd, 1H, $J_{1,8} = 2.6$ Hz, $J_{1,6} = 3.9$ Hz, H-1), 3.74 (s, 3H, CO_2CH_3), 3.56 (dm, 1H, $J_{4,8} = 6.8$ Hz, H-4), 3.42 (ddd, 1H, $J_{1,6} = 3.9$ Hz, $J_{5endo,6} = 5.9$ Hz, $J_{5exo,6} = 9.0$ Hz, H-6), 2.11-2.20 (m, 2H, H-5); ^{13}C NMR 171.4 (C-3), 170.4 (CO_2CH_3), 132.7 (C-8), 119.1 (C-7), 80.8 (C-1), 53.0 (CO_2CH_3), 43.6 (C-4), 42.8 (C-6), 23.8 (C-5).

Methyl 7-bromo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5_{exo}-carboxylate 1H NMR 6.66 (dd, 1H, $J_{1,8} = 2.5$ Hz, $J_{4,8} = 6.9$ Hz, H-8), 5.20 (m, 1H, H-1), 3.81 (dd, $J_{4,5} = 2.3$ Hz, $J_{4,8} = 6.9$ Hz, H-4), 3.76 (s, 3H, CO_2CH_3), 2.83 (ddd, 1H, $J_{4,5} = 2.3$ Hz, $J_{5,6exo} = 5.3$ Hz, $J_{5,6endo} = 10.8$ Hz, H-5), 2.52 (ddd, 1H, $J_{1,6exo} = 3.9$ Hz, $J_{5,6exo} = 5.3$ Hz, $J_{6endo,6exo} = 14.0$ Hz, H-6_{exo}), 2.19 (ddd, 1H, $J_{1,6endo} = 1.7$ Hz, $J_{5,6endo} = 10.8$ Hz, $J_{6endo,6exo} = 14.0$ Hz, H-6_{endo}); ^{13}C NMR 170.4 (CO_2CH_3), 168.9 (C-3), 130.5 (C-8), 123.5 (C-7), 80.8 (C-1), 53.4 (CO_2CH_3), 45.8 (C-4), 39.3 (C-5), 29.7 (C-6); IR 2978, 2924, 2846, 1773, 1734, 1437, 1353, 1265, 1207, 1132, 1009, 801, 737 cm^{-1} ; m/z 263 (49, MH^+ for ^{81}Br), 261 (49, MH^+ for ^{79}Br), 231 [11, (M^+ for $^{81}Br-OMe$)], 229 [11, (M^+ for $^{79}Br-OMe$)], 218 [16, (M^+ for $^{81}Br-CO_2$)], 217 (24), 216 [16, (M^+ for $^{79}Br-CO_2$)], 215 (21), 203 (10), 201 (12), 187 (9), 185 (11), 176 [8, (M^+ for $^{81}Br-86$, retro Diels-Alder)], 174 [9, (M^+ for $^{79}Br-86$, retro Diels-Alder)], 160 (11), 159 [99, (M^+ for $^{81}Br-CO_2-CO_2Me$)], 158 (50), 157 [100, (M^+ for $^{79}Br-CO_2-CO_2Me$)], 156 (45), 147 (11), 145 (11), 137 (45), 93 (32), 78 (44), 77 (64), 65 (5), 60 (8), 59 (11), 55 (11); HRMS calcd for $C_9H_9^{79}BrO_4Na$: 282.95764; found: 282.95723.

Cycloaddition of 5-Iodo-2(H)-pyran-2-one and Methyl Acrylate

A sealed pressure tube (purchased from Aldrich Chemical Co Cat No Z18, 109-9) was charged with 5-iodo-2(H)-pyran-2-one **13** (48 mg, 0.216 mmol), methyl acrylate (0.5 mL, 5.6 mmol, 26 equiv), a few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of 3 isomers of cycloadducts. Silica gel chromatography using 20% v/v ethyl acetate in petrol ether afforded pure samples of the 5-*endo* and 5-*exo* cycloadducts as well a sample of the 6-*endo* product contaminated with traces of the 5-*endo* and 5-*exo* cycloadducts. Combined isolated yield of cycloadducts was 60 mg, 90%.

Methyl 7-iodo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5-*endo*-carboxylate m.p. 97-98 °C; ¹H NMR 6.83 (dd, 1H, J_{1,8} = 2.2 Hz, J_{4,8} = 6.4 Hz, H-8), 5.23 (m, 1H, H-1), 3.85 (dd, 1H, J_{4,5} = 2.7 Hz, J_{4,8} = 6.4 Hz, H-4), 3.73 (s, 3H, CO₂CH₃), 3.04 (dm, 1H, J_{5,6*exo*} = 9.8 Hz, H-5), 2.43 (ddd, 1H, J_{1,6*exo*} = 4.0 Hz, J_{5,6*exo*} = 9.8 Hz, J_{6*exo*,6*endo*} = 14.1 Hz, H-6_{*exo*}), 2.23 (ddd, 1H, J_{1,6*endo*} = 1.5 Hz, J_{5,6*endo*} = 4.0 Hz, J_{6*exo*,6*endo*} = 14.1 Hz, H-6_{*endo*}); ¹³C NMR 171.7 (C-3), 170.6 (CO₂CH₃), 138.0 (C-8), 92.0 (C-7), 83.9 (C-1), 53.24 (CO₂CH₃), 46.7 (C-4), 37.1 (C-5), 29.7 (C-6); IR 3089, 2978, 2924, 2853, 1759, 1734, 1660, 1598, 1456, 1436, 1357, 1302, 1232, 1213, 1158, 1072, 1038, 994, 949, 900, 806, 782, 764, 735, 701, 635, 514 cm⁻¹; m/z 309 (9), 308 (51, M⁺), 277 (18), 264 [41, (M⁺-CO₂)], 205 [80, (M⁺-CO₂-CO₂Me)], 222 [8, (M⁺-86, retro Diels-Alder)], 204 (43), 137 [16, (M⁺-CO₂-I)], 93 (41), 91 (11), 78 (100), 77 (35), 59 (20), 57 (11), 55 (35), 51 (16), 39 (15); HRMS calcd for C₉H₉IO₄Na: 330.94377; found: 330.94272.

Methyl 7-iodo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-6-*endo*-carboxylate ¹H NMR 7.00 (dd, 1H, J_{1,8} = 2.3 Hz, J_{4,8} = 6.7 Hz, H-8), 5.50 (dd, 1H, J_{1,8} = 2.3 Hz, J_{1,6} = 4.0 Hz, H-1), 3.77 (s, 3H, CO₂CH₃), 3.51

(dm, 1H, $J_{4,8} = 6.7$ Hz, H-4), 3.42 (dt, 1H, $J_{5\text{endo},6} = J_{1,6} = 4.0$ Hz, $J_{5\text{exo},6} = 10.6$ Hz, H-6), 2.14 - 2.47 (m, 2H, H-5); ^{13}C NMR 171.7 (C-3), 170.4 ($\underline{\text{CO}_2\text{CH}_3}$), 141.6 (C-8), 92.0 (C-7), 83.2 (C-1), 52.9 (CO_2CH_3), 44.2 (C-4), 43.4 (C-6), 23.5 (C-5).

Methyl 7-iodo-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene-5_{exo}-carboxylate ^1H NMR 6.94 (dd, 1H, $J_{1,8} = 2.3$ Hz, $J_{4,8} = 6.8$ Hz, H-8), 5.23 (dm, 1H, $J_{1,6\text{exo}} = 3.9$ Hz, H-1), 3.75 (s, 3H, CO_2CH_3), 3.69 (dd, $J_{4,5} = 2.3$ Hz, $J_{4,8} = 6.8$ Hz, H-4), 2.78 (ddd, 1H, $J_{4,5} = 2.3$ Hz, $J_{5,6\text{exo}} = 5.3$ Hz, $J_{5,6\text{endo}} = 10.9$ Hz, H-5), 2.44 (ddd, 1H, $J_{1,6\text{exo}} = 3.9$ Hz, $J_{5,6\text{exo}} = 5.3$ Hz, $J_{6\text{endo},6\text{exo}} = 13.6$ Hz, H-6_{exo}), 2.14 (ddd, 1H, $J_{1,6\text{endo}} = 1.6$ Hz, $J_{5,6\text{endo}} = 10.9$ Hz, $J_{6\text{endo},6\text{exo}} = 13.6$ Hz, H-6_{endo}); ^{13}C NMR 170.4 ($\underline{\text{CO}_2\text{CH}_3}$), 168.9 (C-3), 139.3 (C-8), 92.0 (C-7), 83.5 (C-1), 53.3 (CO_2CH_3), 47.1 (C-4), 39.1 (C-5), 29.2 (C-6); IR 2951, 2922, 2852, 1764, 1738, 1597, 1436, 1355, 1209, 1132, 1044, 1003, 897, 803 cm^{-1} ; m/z 309 (9), 308 (51, M^+), 277 (18), 264 [41, ($\text{M}^+ - \text{CO}_2$)], 205 [80, ($\text{M}^+ - \text{CO}_2 - \text{CO}_2\text{Me}$)], 222 [8, ($\text{M}^+ - 86$, retro Diels-Alder)], 204 (43), 137 (16, $\text{M}^+ - \text{CO}_2 - \text{I}$), 93 (41), 91 (11), 78 (100), 77 (35), 59 (20), 57 (11), 55 (35), 51 (16), 39 (15); HRMS calcd for $\text{C}_9\text{H}_9\text{IO}_4\text{Na}$: 330.94377; found: 330.94362.

Cycloaddition of 5-Chloro-2(H)-pyran-2-one and Acrylonitrile

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 5-chloro-2(H)-pyran-2-one **12** (28 mg, 0.21 mmol), acrylonitrile (0.4 mL, 6.0 mmol, 29 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 90 °C. After 4 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of cycloadducts. Silica gel chromatography, using 25% v/v ethyl acetate in petroleum ether afforded samples of the 5-*endo*, 5-*exo*

and 6-*endo* cycloadducts as well as a sample of the 6-*exo* cycloadduct contaminated with the 5-*exo* cycloadduct. Combined isolated yield of cycloadducts was 40 mg, 100%.

7-Chloro-5_{endo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 127 °C; ¹H NMR 6.53 (dd, 1H, J_{1,8} = 2.3 Hz, J_{4,8} = 6.6 Hz, H-8), 5.18 (ddd, 1H, J_{1,6endo} = 1.5 Hz, J_{1,8} = 2.3 Hz, J_{1,6exo} = 3.8 Hz, H-1), 3.88 (dd, 1H, J_{4,5} = 3.2 Hz, J_{4,8} = 6.6 Hz, H-4), 3.24 (dt, 1H, J_{4,5} = 3.2 Hz, J_{5,6endo} = 3.7 Hz, J_{5,6exo} = 9.5 Hz, H-5), 2.72 (ddd, 1H, J_{1,6exo} = 3.8 Hz, J_{5,6exo} = 9.5 Hz, J_{6exo,6endo} = 14.0 Hz, H-6_{exo}), 2.19 (ddd, 1H, J_{1,6endo} = 1.5 Hz, J_{5,6endo} = 3.7 Hz, J_{6exo,6endo} = 14.0 Hz, H-6_{endo}); ¹³C NMR 168.4 (C-3), 136.6 (C-7), 124.0 (C-8), 119.0 (CN), 78.6 (C-1), 44.1 (C-4), 31.9 (C-6), 23.7 (C-5); IR 2925, 2854, 2248, 1766, 1621, 1442, 1374, 1342, 1266, 1166, 1069, 1028, 986, 904, 867, 820, 808, 741, 705, 664, 637 cm⁻¹; m/z 185 (4, M⁺ for ³⁷Cl), 184 (4), 183 (10, M⁺ for ³⁵Cl), 141 [10, (M⁺ for ³⁷Cl-CO₂)], 139 [29, (M⁺ for ³⁵Cl-CO₂)], 130 [18, (M⁺ - 86, retro Diels-Alder)], 105 (12), 104 [100, (M⁺-CO₂-Cl)], 103 (10), 102 (27), 99 (13), 78 (7), 77 (33), 51 (14).

7-Chloro-6_{endo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR (CDCl₃) 6.62 (dd, 1H, J_{1,8} = 2.5 Hz, J_{4,8} = 7.0 Hz, H-8), 5.27 (m, 1H, H-1), 3.67 (dm, 1H, J_{4,8} = 7.0 Hz, H-4), 3.45 (ddd, 1H, J_{1,6} = 4.1 Hz, J_{5endo,6} = 5.0 Hz, J_{5exo,6} = 9.5 Hz, H-6), 2.48 (ddd, 1H, J_{4,5exo} = 2.7 Hz, J_{5exo,6} = 9.5 Hz, J_{5endo,5exo} = 13.4 Hz, H-5_{exo}), 2.00 (ddd, 1H, J_{4,5endo} = 2.7 Hz, J_{5endo,6} = 5.0 Hz, J_{5endo,5exo} = 13.4 Hz, H-5_{endo}); IR 2959, 2927, 2855, 2248, 1778, 1670, 1645, 1624, 1529, 1455, 1361, 1266, 1237, 1209, 1138, 1071, 1005, 926, 912, 802, 779, 738, 705, 624, 507 cm⁻¹; m/z 185 (4, M⁺ for ³⁷Cl), 184 (4), 183 (8, M⁺ for ³⁵Cl), 141 [6, (M⁺ for ³⁷Cl-CO₂)], 139 [15, (M⁺ for ³⁵Cl-CO₂)], 130 [27, (M⁺-86, retro Diels-Alder)], 105 (10), 104 [100, (M⁺-CO₂-Cl)], 103 (7), 102 (25), 99 (8), 78 (5), 77 (22), 57 (16).

7-Chloro-5_{exo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 108-110 °C; ¹H NMR (CDCl₃) 6.42 (dd, 1H, J_{1,8} = 2.4 Hz, J_{4,8} = 6.8 Hz, H-8), 5.17 (m, 1H, Hz, H-1), 3.84 (dd, 1H, J_{4,5} = 2.2 Hz, J_{4,8} = 6.8

Hz, H-4), 2.94 (ddd, 1H, $J_{4,5} = 2.2$ Hz, $J_{5,6\text{exo}} = 5.2$ Hz, $J_{5,6\text{endo}} = 10.8$ Hz, H-5), 2.55 (dm, 1H, $J_{6\text{exo},6\text{endo}} = 13.8$ Hz, H-6_{exo}), 2.41 (ddd, 1H, $J_{1,6\text{endo}} = 1.1$ Hz, $J_{5,6\text{endo}} = 10.8$ Hz, $J_{6\text{exo},6\text{endo}} = 13.8$ Hz, H-6_{endo}); ^{13}C NMR (CDCl_3) 167.7 (C-3), 136.5 (C-7), 124.9 (C-8), 118.7 (CN), 78.5 (C-1), 44.6 (C-4), 31.4 (C-6), 24.2 (C-5); IR 2922, 2851, 2245, 1770, 1627, 1448, 1361, 1183, 1132, 1051, 1010, 961, 909, 859, 794, 685, 640 cm^{-1} ; m/z (EI) 185 (2, M^+ for ^{37}Cl), 184 (9, MH^+ for ^{35}Cl), 183 (3, M^+ for ^{35}Cl), 141 [16, (M^+ for $^{37}\text{Cl-CO}_2$)], 139 [46, (M^+ for $^{35}\text{Cl-CO}_2$)], 130 [23, ($\text{M}^+ - 86$, retro Diels-Alder)], 105 (19), 104 [100, ($\text{M}^+ - \text{CO}_2 - \text{Cl}$)], 103 (15), 102 (35), 99 (22), 78 (11), 77 (52), 76 (14), 75 (11), 73 (13), 51 (10), 50 (13), 39 (19), 38 (11); HRMS calcd for $\text{C}_8\text{H}_6\text{ClNO}_2\text{Na}$: 205.9980; found: 205.99775; Anal calcd for $\text{C}_8\text{H}_6\text{ClNO}_2$: C, 52.34, H, 3.29, N, 7.63; found: C, 52.20, H, 3.38, N, 7.44.

7-Chloro-6_{exo}-cyano-2-oxabicyclo[2.2.2]oct-7-en-3-one ^1H NMR 6.49 (dd, 1H, $J_{1,8} = 2.5$ Hz, $J_{4,8} = 6.9$ Hz, H-8), 5.25 (m, 1H, H-1), 3.68 (dm, 1H, $J_{4,8} = 6.9$ Hz, H-4), 3.10 (dd, 1H, $J_{5\text{exo},6} = 4.5$ Hz, $J_{5\text{endo},6} = 10.9$ Hz, H-6), 2.08- 2.19 (m, 2H, H-5).

Cycloaddition of 5-Bromo-2(H)-pyran-2-one and Acrylonitrile

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 5-bromo-2(H)-pyran-2-one **5** (80 mg, 0.46 mmol), acrylonitrile (0.6 mL, 9.1 mmol, 20 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of four cycloadducts. Silica gel chromatography, using 25% v/v ethyl acetate in petroleum ether afforded samples of the 5-*endo*, 5-*exo* and 6-*endo* cycloadducts as well as a sample of the 6-*exo* cycloadduct contaminated with the 5-*exo* cycloadduct. Combined isolated yield of cycloadducts was 101 mg, 96%.

7-Bromo-5_{endo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 126 °C; ¹H NMR 6.75 (dd, 1H, J_{1,8} = 2.4 Hz, J_{4,8} = 6.6 Hz, H-8), 5.24 (dm, 1H, J_{1,6_{exo}} = 3.7 Hz, H-1), 3.87 (dd, 1H, J_{4,5} = 3.2 Hz, J_{4,8} = 6.6 Hz, H-4), 3.22 (dt, 1H, J_{5,6_{endo}} = 3.2 Hz, J_{5,6_{exo}} = 9.5 Hz, H-5), 2.69 (ddd, 1H, J_{1,6_{exo}} = 3.7 Hz, J_{5,6_{exo}} = 9.5 Hz, J_{6_{endo},6_{exo}} = 14.0 Hz, H-6_{exo}), 2.17 (ddd, 1H, J_{1,6_{endo}} = 1.5 Hz, J_{5,6_{endo}} = 3.7 Hz, J_{6_{endo},6_{exo}} = 14.0 Hz, H-6_{endo}); ¹³C NMR 168.1 (C-3), 128.7 (C-8), 123.7 (C-7), 119.0 (CN), 80.1 (C-1), 45.1 (C-4), 31.8 (C-6), 23.4 (C-5); IR 2923, 2852, 2248, 1765, 1615, 1446, 1357, 1276, 1166, 1060, 1009, 984, 897, 863, 742, 652, 631, 544 cm⁻¹; m/z 229 (8, M⁺ for ⁸¹Br), 227 (8, M⁺ for ⁷⁹Br), 185 [16, (M⁺ for ⁸¹Br-CO₂)], 183 [16, (M⁺ for ⁷⁹Br-CO₂)], 105 (10), 104 (100, M⁺-CO₂-Br), 77 (33), 51 (10), 39 (9); HRMS calcd for C₈H₆⁸¹BrO₂Na: 251.94537; found: 251.94580.

7-Bromo-6_{endo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene m.p. 93 °C; ¹H NMR 6.85 (dd, 1H, J_{1,8} = 2.6 Hz, J_{4,8} = 6.9 Hz, H-8), 5.35 (dd, 1H, J_{1,8} = 2.6 Hz, J_{1,6} = 3.5 Hz, H-1), 3.66 (dm, 1H, J_{4,8} = 6.9 Hz, H-4), 3.46 (ddd, 1H, J_{1,6} = 3.8 Hz, J_{5_{endo},6} = 5.0 Hz, J_{5_{exo},6} = 9.5 Hz, H-6), 2.46 (ddd, 1H, J_{4,5_{exo}} = 2.7 Hz, J_{5_{exo},6} = 9.5 Hz, J_{5_{exo},5_{endo}} = 13.3 Hz, H-5_{exo}), 1.99 (ddd, 1H, J_{4,5_{endo}} = 2.7 Hz, J_{5_{endo},6} = 5.0 Hz, J_{5_{endo},5_{exo}} = 13.3 Hz, H-5_{endo}); ¹³C NMR 169.5 (C-3), 132.9 (C-8), 119.2 (CN), 117.5 (C-7), 79.3 (C-1), 42.1 (C-4), 28.6 (C-6), 26.4 (C-5); IR 2922, 2852, 2248, 1772, 1455, 1360, 1266, 1208, 1136, 1060, 997, 926, 798, 736, 698 cm⁻¹; m/z 229 (13, M⁺ for ⁸¹Br), 227 (12, M⁺ for ⁷⁹Br), 185 [25, (M⁺ for ⁸¹Br-CO₂)], 183 [25, (M⁺ for ⁷⁹Br-CO₂)], 176 [27, (M⁺ for ⁸¹Br-53, retro Diels-Alder)], 174 [28, (M⁺ for ⁷⁹Br-53, retro Diels-Alder)], 147 (23), 145 (23), 105 (18), 104 (100, M⁺-CO₂-Br), 103 (11), 78 (13), 77 (62), 51 (9); HRMS calcd for C₈H₆⁸¹BrO₂Na: 251.94537; found: 251.94607.

7-Bromo-5_{exo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-en-3-one m.p. 133 °C; ¹H NMR 6.65 (dd, 1H, J_{1,8} = 2.4 Hz, J_{4,8} = 6.8 Hz, H-8), 5.24 (m, 1H, H-1), 3.83 (dd, 1H, J_{4,5} = 2.4 Hz, J_{4,8} = 6.8 Hz, H-4), 2.94 (ddd, 1H, J_{4,5} = 2.4 Hz, J_{5,6_{exo}} = 5.2 Hz, J_{5,6_{endo}} = 10.7 Hz, H-5), 2.52 (ddd, 1H, J_{1,6_{exo}} = 3.8

Hz, $J_{5,6\text{exo}} = 5.2$ Hz, $J_{6\text{exo},6\text{endo}} = 14.0$ Hz, H-6_{exo}), 2.39 (ddd, 1H, $J_{1,6\text{endo}} = 1.6$ Hz, $J_{5,6\text{endo}} = 10.7$ Hz, $J_{6\text{exo},6\text{endo}} = 14.0$ Hz, H-6_{endo}); ^{13}C NMR 166.0 (C-3), 128.1 (C-8), 122.3 (CN), 117.2 (C-7), 78.5 (C-1), 44.2 (C-4), 29.9 (C-6), 22.5 (C-5); IR 2952, 2919, 2852, 2241, 1770, 1617, 1446, 1359, 1180, 1132, 1038, 1007, 957, 929, 907, 862, 794, 657, 636 cm^{-1} ; m/z 230 (15, MH^+ for ^{81}Br), 228 (15, MH^+ for ^{79}Br), 203 (11), 201 (11), 185 [39, (M^+ for $^{81}\text{Br-CO}_2$)], 183 [40, (M^+ for $^{79}\text{Br-CO}_2$)], 176 [6, (M^+ for $^{81}\text{Br-53}$, retro Diels-Alder)], 174 [6, (M^+ for $^{79}\text{Br-53}$, retro Diels-Alder)], 147 (8), 145 (8), 105 (13), 104 (100), 103 (8), 78 (6), 77 (26), 51 (9); HRMS calcd for $\text{C}_8\text{H}_6^{81}\text{BrNO}_2\text{Na}$: 251.94537; found: 251.94527.

7-Bromo-6_{exo}-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ^1H NMR 6.71 (dd, 1H, $J_{1,8} = 2.4$ Hz, $J_{4,8} = 6.8$ Hz, H-8), 5.32 (m, 1H, $J = 1.6$ Hz, H-1), 3.68 (dt, 1H, $J_{4,5\text{endo}} = 2.7$ Hz, $J_{4,8} = 6.8$ Hz, H-4), 3.10 (ddd, 1H, $J_{1,6} = 1.2$ Hz, $J_{5\text{exo},6} = 3.7$ Hz, $J_{5\text{endo},6} = 10.0$ Hz, H-6), 2.14- 2.26 (m, 2H, H-5).

Cycloaddition of 5-Iodo-2(H)-pyran-2-one and Acrylonitrile

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 5-iodo-2(H)-pyran-2-one **13** (41 mg, 0.185 mmol), acrylonitrile (0.5 mL, 7.6 mmol, 41 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 4 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of four cycloadducts. Silica gel chromatography, using 25% v/v ethyl acetate in petroleum ether afforded samples of the 5-*endo* and 6-*endo* cycloadducts as well as a mixed sample of the 5-*endo* and 6-*exo* cycloadducts. Combined isolated yield of cycloadducts was 28 mg, 55%.

7-Iodo-5_{endo}-cyano-2-oxabicyclo[2.2.2]oct-7-en-3-one ^1H NMR 7.03 (dd, 1H, $J_{1,8} = 2.1$ Hz, $J_{4,8} =$

6.4 Hz, H-8), 5.23 (m, 1H, H-1), 3.78 (dd, 1H, $J_{4,5} = 2.6$ Hz, $J_{4,8} = 6.4$ Hz, H-4), 3.18 (dm, 1H, $J_{5,6\text{exo}} = 9.5$ Hz, H-5), 2.60 (ddd, 1H, $J_{1,6\text{exo}} = 3.8$ Hz, $J_{5,6\text{exo}} = 9.6$ Hz, $J_{6\text{endo},6\text{exo}} = 14.0$ Hz, H-6_{exo}), 2.14 (ddd, 1H, $J_{1,6\text{endo}} = 1.3$ Hz, $J_{5,6\text{endo}} = 3.6$ Hz, $J_{6\text{endo},6\text{exo}} = 14.0$ Hz, H-6_{endo}); ^{13}C NMR 166.6 (C-3), 135.8 (C-8), 117.6 (CN), 92.2 (C-7), 81.7 (C-1), 44.7 (C-4), 29.9 (C-6), 21.8 (C-5); IR 2978, 2923, 2852, 2246, 1765, 1659, 1464, 1358, 1263, 1181, 1132, 1029, 1001, 903, 792, 740, 632 cm^{-1} ; m/z 276 (3), 275 (14, M^+), 231 [47, ($\text{M}^+ - \text{CO}_2$)], 222 (5), 194 (7), 105 (9), 104 (100), 78 (15), 77 (50), 51 (12); HRMS calcd for $\text{C}_8\text{H}_6\text{INO}_2\text{Na}$: 297.93355; found: 297.93356.

7-Iodo-6-endo-cyano-2-oxabicyclo[2.2.2]oct-7-en-3-one ^1H NMR 7.14 (dd, 1H, $J_{1,8} = 2.3$ Hz, $J_{4,8} = 6.7$ Hz, H-8), 5.41 (dd, 1H, $J_{1,8} = 2.3$ Hz, $J_{1,6} = 3.6$ Hz, H-1), 3.58 (dt, 1H, $J_{4,5\text{exo}} = 2.7$ Hz, $J_{4,8} = 6.7$ Hz, H-4), 3.44 (ddd, 1H, $J_{1,6} = 3.6$ Hz, $J_{5\text{endo},6} = 5.0$ Hz, $J_{5\text{exo},6} = 9.5$ Hz, H-6), 2.43 (ddd, 1H, $J_{4,5\text{exo}} = 3.1$ Hz, $J_{5\text{exo},6} = 9.5$ Hz, $J_{5\text{endo},5\text{exo}} = 13.2$ Hz, H-5_{exo}), 1.97 (ddd, 1H, $J_{4,5\text{endo}} = 2.7$ Hz, $J_{5\text{endo},6} = 5.0$ Hz, $J_{5\text{endo},5\text{exo}} = 13.2$ Hz, H-5_{endo}).

7-Iodo-5-exo-cyano-2-oxabicyclo[2.2.2]oct-7-en-3-one m.p. 136 °C; ^1H NMR 6.93 (dd, 1H, $J_{1,8} = 2.2$ Hz, $J_{4,8} = 6.7$ Hz, H-8), 5.29 (m, 1H, H-1), 3.74 (dd, 1H, $J_{4,5} = 2.3$ Hz, $J_{4,8} = 6.7$ Hz, H-4), 2.88 (ddd, 1H, $J_{4,5} = 2.3$ Hz, $J_{5,6\text{exo}} = 5.4$ Hz, $J_{5,6\text{endo}} = 10.8$ Hz, H-5), 2.44 (ddd, 1H, $J_{1,6\text{exo}} = 3.8$ Hz, $J_{5,6\text{exo}} = 5.4$ Hz, $J_{6\text{endo},6\text{exo}} = 14.0$ Hz, H-6_{exo}), 2.35 (ddd, 1H, $J_{1,6\text{endo}} = 1.5$ Hz, $J_{5,6\text{endo}} = 10.8$ Hz, $J_{6\text{endo},6\text{exo}} = 14.0$ Hz, H-6_{endo}); ^{13}C NMR 165.7 (C-3), 136.7 (C-8), 117.0 (CN), 92.4 (C-7), 81.4 (C-1), 45.3 (C-4), 26.7 (C-5), 21.6 (C-6); IR 2947, 2923, 2852, 2241, 1762, 1594, 1443, 1357, 1270, 1253, 1159, 1054, 1032, 982, 894, 863, 797, 733 cm^{-1} ; m/z 276 (7), 275 (51, M^+), 231 [46, ($\text{M}^+ - \text{CO}_2$)], 194 (10), 148 [7, ($\text{M}^+ - \text{I}$)], 105 (9), 104 (100), 78 (15), 77 (48), 51 (13), 39 (12); HRMS calcd for $\text{C}_8\text{H}_6\text{INO}_2\text{Na}$: 297.93355; found: 297.93096.

7-Iodo-6_{exo}-cyano-2-oxabicyclo[2.2.2]oct-7-en-3-one ¹H NMR ppm 6.99 (dd, 1H, $J_{1,8} = 2.3$ Hz, $J_{4,8} = 6.4$ Hz, H-8), 5.37 (m, 1H, H-1), 3.60 (dt, 1H, $J_{4,5endo} = 2.7$ Hz, $J_{4,8} = 6.4$ Hz, H-4), 3.03 (ddd, 1H, $J_{1,6} = 1.4$ Hz, $J_{5exo,6} = 5.0$ Hz, $J_{5endo,6} = 10.0$ Hz, H-6), 2.15 (m, 2H, H-5).

Cycloaddition of 5-Chloro-2(H)-pyran-2-one and Vinylene carbonate

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 5-chloro-2(H)-pyran-2-one **12** (15 mg, 0.116 mmol), vinylene carbonate (0.5 mL, 7.9 mmol, 70 equiv), dichloromethane (ca 1.0 mL), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 14 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two cycloadducts. Pure samples of the *endo* and *exo* cycloadducts were obtained by silica gel chromatography, using 30% v/v ethyl acetate in petroleum ether. Combined isolated yield of cycloadducts was 10 mg, 42%.

endo isomer ¹H NMR 6.47 (dd, 1H, $J_{1,8} = 2.5$ Hz, $J_{4,8} = 6.6$ Hz, H-8), 5.36 (dd, 1H, $J_{1,8} = 2.5$ Hz, $J_{1,6} = 4.2$ Hz, H-1), 5.21 (dd, 1H, $J_{1,6} = 4.2$ Hz, $J_{5,6} = 7.7$ Hz, H-6), 5.07 (dd, 1H, $J_{4,5} = 3.7$ Hz, $J_{5,6} = 7.7$ Hz, H-5), 4.13 (dd, 1H, $J_{4,5} = 3.7$ Hz, $J_{4,8} = 6.6$ Hz, H-4); ¹³C NMR 165.2 (CO, lactone), 152.4 (CO, carbonate), 132.9 (C-7), 123.2 (C-8), 77.4 (C-5), 72.7 (C-6), 70.3 (C-1), 45.6 (C-4); IR 2918, 2956, 1846, 1813, 1781, 1621, 1374, 1261, 1164, 1097, 1066, 1004, 870, 809, 760, 738, 712 cm⁻¹; m/z 218 (3), 217 (2), 216 (9, M⁺), 132 (50), 130 (100), 115 (19), 104 (16), 102 (52), 100 (17), 73 (10), 65 (18), 51 (16); HRMS calcd for C₈H₅³⁵ClO₅Na: 238.97177; found: 238.97246.

exo isomer ^1H NMR 6.38 (dd, 1H, $J_{1,8} = 2.3$ Hz, $J_{4,8} = 7.0$ Hz, H-8), 5.29 (t, 1H, $J_{1,8} = 2.0$ Hz, H-1), 4.94 (dd, 1H, $J_{1,6} = 2.0$ Hz, $J_{5,6} = 8.5$ Hz, H-6), 4.89 (dd, 1H, $J_{4,5} = 3.8$ Hz, $J_{5,6} = 8.5$ Hz, H-5), 4.11 (dd, 1H, $J_{4,5} = 3.8$ Hz, $J_{4,8} = 7.0$, H-4); ^{13}C NMR 164.0 (CO, lactone), 152.2 (CO, carbonate), 132.6 (C-7), 123.3 (C-8), 78.9 (C-1), 72.8 (C-6), 70.8 (C-5), 45.9 (C-4); IR 2962, 2918, 1846, 1816, 1618, 1463, 1355, 1261, 1163, 1093, 1045, 938, 800, 761 cm^{-1} ; m/z 217 (4, MH^+), 172 (18, $\text{M}^+ - \text{CO}_2$), 142 (22), 132 (32), 131 (9), 130 [100, ($\text{M}^+ - 86$, retro Diels-Alder)], 128 (20), 117 (13), 116 (12), 115 (37), 104 (16), 102 (57), 100 (43), 97 (15), 87 (19), 85 (14), 83 (16), 81 (21), 74 (11), 73 (15), 72 (23), 71 (18), 69 (18), 65 (30), 59 (30), 57 (27), 55 (23); HRMS calcd for $\text{C}_8\text{H}_5^{35}\text{ClO}_5\text{Na}$: 238.97177; found: 238.97207.

Cycloaddition of 5-Bromo-2(H)-pyran-2-one and Vinylene carbonate

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 5-bromo-2(H)-pyran-2-one **5** (104 mg, 0.594 mmol), vinylene carbonate (1.0 mL, 15.8 mmol, 27 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 14 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two cycloadducts. Pure samples of the *endo* and *exo* cycloadducts were obtained by silica gel chromatography, using 20-60% v/v ethyl acetate in petroleum ether. Combined isolated yield of cycloadducts was 66 mg, 43 %.

endo isomer m.p. 140-145 °C (dec) ^1H NMR 6.71 (dd, 1H, $J_{1,8} = 2.6$ Hz, $J_{4,8} = 6.6$ Hz, H-8), 5.44 (dd, 1H, $J_{1,8} = 2.6$ Hz, $J_{1,6} = 4.3$ Hz, H-1), 5.21 (dd, 1H, $J_{1,6} = 4.3$ Hz, $J_{5,6} = 7.6$ Hz, H-6), 5.06 (dd,

1H, $J_{4,5} = 3.7$ Hz, $J_{5,6} = 7.6$ Hz, H-5), 4.14 (dd, 1H, $J_{4,5} = 3.7$ Hz, $J_{4,8} = 6.6$ Hz, H-4); ^{13}C NMR 164.9 (C-3), 152.4 (CO, carbonate), 128.0 (C-8), 119.6 (C-7), 78.5 (C-1), 72.9 (C-6), 70.1 (C-5), 46.7 (C-4); IR 2925, 2849, 1844, 1807, 1774, 1703, 1373, 1226, 1160, 1094, 1061, 995, 925, 868, 802, 755, 731, 689, 623 cm^{-1} ; m/z 262 (36, M^+ for ^{81}Br), 260 (36, M^+ for ^{79}Br), 256 (13), 218 (14, $\text{M}^+ - \text{CO}_2$), 216 (14, $\text{M}^+ - \text{CO}_2$), 177 (17), 176 [100, ($\text{M}^+ - 86$, retro Diels-Alder)], 175 (19), 174 [100, ($\text{M}^+ - 86$, retro Diels-Alder)], 167 (23), 161 (11), 159 (11), 148 (33), 147 (40), 145 (48), 144 (10), 129 (14), 125 (11), 113 (14), 112 (13), 111 (15), 109 (12), 104 (13), 99 (10), 98 (10), 97 (20), 96 (11), 95 (11), 93 (16), 85 (16), 84 (11), 83 (16), 82 (10), 81 (17), 73 (13), 71 (22), 70 (10), 65 (20), 60 (10), 57 (28); Anal calcd for $\text{C}_8\text{H}_5\text{BrO}_5$: C, 36.81, H, 1.93; found: C, 36.95, H, 1.88.

exo isomer ^1H NMR 6.61 (dd, 1H, $J_{1,8} = 2.3$ Hz, $J_{4,8} = 6.9$ Hz, H-8), 5.36 (t, 1H, $J_{1,8} = 2.0$ Hz, $J_{1,6} = 2.0$ Hz, H-1), 4.93 (dd, 1H, $J_{1,6} = 1.9$ Hz, $J_{5,6} = 8.5$ Hz, H-6), 4.88 (dd, 1H, $J_{4,5} = 3.7$ Hz, $J_{5,6} = 8.5$ Hz, H-5), 4.10 (dd, 1H, $J_{4,5} = 3.7$ Hz, $J_{4,8} = 6.9$ Hz, H-4); ^{13}C NMR 164.6 (C-3), 152.3 (CO, carbonate), 127.9 (C-8), 120.5 (C-7), 80.2 (C-1), 72.6 (C-6), 70.3 (C-5), 46.9 (C-4); IR 2955, 2924, 2849, 1793, 1703, 1354, 1264, 1226, 1165, 1085, 1052, 1033, 1009, 991, 929, 736 cm^{-1} ; m/z 262 (5, M^+ for ^{81}Br), 260 (5, M^+ for ^{79}Br), 218 (26, $\text{M}^+ - \text{CO}_2$), 216 (26, $\text{M}^+ - \text{CO}_2$), 189 (15), 187 (14), 176 (81, $\text{M}^+ - 86$, retro Diels-Alder), 175 (9), 174 (100, $\text{M}^+ - 86$, retro Diels-Alder), 161 (24), 159 (24), 147 (35), 145 (54), 144 (27), 133 (12), 131 (13), 109 (16), 93 (34), 81 (23), 65 (48), 63 (12), 59 (14), HRMS calcd for $\text{C}_8\text{H}_5^{81}\text{BrO}_5\text{Na}$: 284.91921; found: 284.91948.

Cycloaddition of 5-Iodo-2(H)-pyran-2-one and Vinylene carbonate

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 5-iodo-2(H)-pyran-2-one **13** (39 mg, 0.175 mmol), vinylene carbonate (0.5 mL, 7.9 mmol, 45 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic

stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 14 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two cycloadducts. Pure samples of the *endo* and *exo* cycloadducts were obtained by silica gel chromatography, using 30% v/v ethyl acetate in petroleum ether. Combined isolated yield of cycloadducts was 21mg, 39%.

endo isomer m.p. 146 (dec.) °C; ¹H NMR 7.00 (dd, 1H, J_{1,8} = 2.1 Hz, J_{4,8} = 6.4 Hz, H-8), 5.52 (dd, 1H, J_{1,8} = 2.3 Hz, J_{1,6} = 4.3 Hz, H-1), 5.19 (dd, 1H, J_{1,6} = 4.3 Hz, J_{5,6} = 7.6 Hz, H-6), 5.04 (dd, 1H, J_{4,5} = 3.7 Hz, J_{5,6} = 7.6 Hz, H-5), 4.09 (dd, 1H, J_{4,5} = 3.7 Hz, J_{4,8} = 6.4 Hz, H-4); ¹³C NMR 164.0 (C-3), 152.5 (CO, carbonate), 137.1 (C-8), 88.8 (C-7), 81.3 (C-1), 73.4 (C-6), 70.3 (C-5), 48.3 (C-4); IR 2923, 2851, 1843, 1796, 1769, 1594, 1463, 1371, 1264, 1161, 1094, 1059, 1024, 990, 865, 803, 758, 733 cm⁻¹; m/z 309 (7), 308 (34, M⁺), 264 [21, (M⁺-CO₂)], 223 (11), 222 [100, (M⁺-86, retro Diels-Alder)], 220 (10), 207 (10), 194 (37), 127 (11, I), 95 (13), 94 (9), 93 (45), 65 (31), 59 (10), 52 (14), 51 (17), 50 (15); HRMS calcd for C₈H₅IO₅Na: 330.90739; found: 330.90796.

exo isomer m.p. 159-164 °C (dec); ¹H NMR 6.90 (dd, 1H, J_{1,8} = 2.2 Hz, J_{4,8} = 6.8 Hz, H-8), 5.40 (t, 1H, J_{1,8} = J_{1,6} = 2.0 Hz, H-1), 4.90 (dd, 1H, J_{1,6} = 1.8 Hz, J_{5,6endo} = 8.5 Hz, H-6), 4.84 (dd, 1H, J_{4,5endo} = 3.8 Hz, J_{5,6endo} = 8.5 Hz, H-5), 4.03 (dd, 1H, J_{4,5} = 3.8 Hz, J_{4,8} = 6.8 Hz, H-4); ¹³C NMR 163.4 (C-3), 152.5 (CO, carbonate), 135.3 (C-8), 88.8 (C-7), 82.1 (C-1), 70.9 (C-6), 68.8 (C-5), 47.2 (C-4); IR 2978, 2923, 2852, 1844, 1813, 1778, 1464, 1354, 1262, 1161, 1087, 1055, 1025, 1005, 931, 852, 757, 670 cm⁻¹; m/z 309 (9), 308 (4, M⁺), 264 [27, (M⁺-CO₂)], 223 (4), 222 [16, (M⁺-86, retro Diels-Alder)], 220 (19), 207 (10), 194 (18), 179 (10), 127 (27, I), 95 (5), 94 (7), 93 (100), 81 (11), 65 (63), 64 (11), 63 (20), 62 (13), 54 (10), 52 (11), 51 (26), 50 (19); HRMS calcd for C₈H₅IO₅Na: 330.90739; found: 330.90645.

Cycloaddition of 5-Chloro-2(H)-pyran-2-one and (2-Chloroethyl) vinyl ether

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 5-Chloro-2(H)-pyran-2-one **12** (32 mg, 0.25 mmol), (2-chloroethyl) vinyl ether (0.4 mL, 4.9 mmol, 16 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 90 °C. After 4 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two cycloadducts. Silica gel chromatography, using 10-30% v/v ethyl acetate in petroleum ether afforded a pure sample of the 5-*endo* cycloadduct as well as a mixed sample of the 5-*endo* and 5-*exo* cycloadducts. Combined isolated yield of cycloadducts was 41 mg, 70%.

7-Chloro-5_{endo}-(2-chloroethoxy)-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.26 (dd, 1H, J_{1,8} = 2.4 Hz, J_{4,8} = 6.5 Hz, H-8), 5.07 (ddd, 1H, J_{1,6endo} = 1.7 Hz, J_{1,8} = 2.4 Hz, J_{1,6exo} = 3.8 Hz, H-1), 4.08 (dm, 1H, J_{5,6exo} = 7.8 Hz, H-5), 3.94 (dd, 1H, J_{4,5} = 3.2 Hz, J_{4,8} = 6.5 Hz, H-4), 3.72 (m, 2H, OCH₂CH₂Cl), 3.58 (t, 2H, J = 5.5 Hz, OCH₂CH₂Cl), 2.63 (ddd, 1H, J_{1,6exo} = 3.8 Hz, J_{5,6exo} = 7.8 Hz, J_{6exo,6endo} = 14.3 Hz, H-6_{exo}), 1.82 (dm, 1H, J_{6exo,6endo} = 14.3 Hz, H-6_{endo}); ¹³C NMR 170.6 (C-3), 133.7 (C-7), 123.2 (C-8), 79.4 (C-1), 72.2 (C-5), 69.8 (OCH₂CH₂Cl), 47.7 (C-4), 43.0 (OCH₂CH₂Cl), 35.6 (C-6); IR 2919, 2852, 1766, 1625, 1432, 1357, 1267, 1161, 1114, 1023, 994, 919, 873, 736 cm⁻¹; m/z 238 (9), 236 (13, M⁺), 132 (31), 131 (11), 130 [94, (M⁺-106, retro Diels-Alder)], 108 (83), 107 (13), 106 [100, (M⁺-130, retro Diels-Alder)], 104 (16), 102 (48), 95(5), 78 (5), 77 (29), 65 (23), 63 (54), 62 (25), HRMS calcd for C₉H₁₀³⁵Cl₂O₃Na: 258.98992; found: 258.98945; Anal calcd for C₉H₁₀Cl₂O₃: C, 45.60, H, 4.25; found: C, 45.80, H, 4.39.

7-Chloro-5_{exo}-(2-chloroethoxy)-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.24 (dd, 1H, J_{1,8} = 2.6 Hz, J_{4,8} = 7.1 Hz, H-8), 5.01 (m, 1H, H-1), 3.95 (dm, 1H, J_{5,6endo} = 8.8 Hz, H-5), 3.82 (dd, 1H, J_{4,5} = 3.2 Hz, J_{4,8} = 7.1 Hz, H-4), 3.61 (m, 4H, OCH₂CH₂Cl), 2.34 (ddd, 1H, J_{1,6endo} = 1.6 Hz, J_{5,6endo} = 8.8 Hz, J_{6exo,6endo} = 14.1 Hz, H-6_{endo}), 2.09 (dt, 1H, J_{1,6exo} = J_{5,6exo} = 3.4 Hz, J_{6exo,6endo} = 14.1 Hz, H-6_{exo}); ¹³C NMR 169.7 (C-3), 136.8 (C-7), 122.9 (C-8), 79.4 (C-1), 74.3 (C-5), 69.8 (OCH₂CH₂Cl), 47.5 (C-4), 42.8 (OCH₂CH₂Cl), 34.2 (C-6).

Cycloaddition of 5-Bromo-2(H)-pyran-2-one and (2-Chloroethyl) vinyl ether

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 5-bromo-2(H)-pyran-2-one **5** (128 mg, 0.731 mmol), (2-chloroethyl) vinyl ether (0.7 mL, 8.6 mmol, 12 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two cycloadducts. Silica gel chromatography, using 20% v/v ethyl acetate in petroleum ether gave a pure sample of the 5-*endo* and 5-*exo* cycloadducts, 166 mg, 81%.

7-Bromo-5_{endo}-(2-chloroethoxy)-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene and **7-Bromo-5_{exo}-(2-chloroethoxy)-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene** ¹H NMR 5-*endo* cycloadduct 6.47 (dd, 1H, J_{1,8} = 2.3 Hz, J_{4,8} = 6.4 Hz, H-8), 5.13 (dt, 1H, J_{1,6endo} = 2.0 Hz, J_{1,6exo} = 3.8 Hz, H-1), 4.06 (dt, 1H, J_{4,5} = 2.6 Hz, J_{5,6endo} = 7.9 Hz, H-5), 3.84 (dd, 1H, J_{4,5} = 3.3 Hz, J_{4,8} = 6.4 Hz, H-4), 3.70 (m, 2H, OCH₂CH₂Cl), 3.57 (dd, 2H, J = 5.5 Hz, 11.6 Hz, OCH₂CH₂Cl), 2.60 (ddd, 1H, J_{1,6exo} = 3.9 Hz, J_{5,6exo} = 7.8 Hz, J_{6exo,6endo} = 14.3 Hz, H-6_{exo}), 1.80 (dm, 1H, J_{6exo,6endo} = 14.3 Hz, H-6_{endo}) 5-*exo*

cycloadduct 6.61 (dd, 1H, $J_{1,8} = 2.5$ Hz, $J_{4,8} = 6.8$ Hz, H-8), 5.07 (m, 1H, H-1), 3.89 (dm, 1H, $J_{5,6endo} = 8.8$ Hz, H-5), 3.82 (dd, 1H, $J_{4,5} = 3.2$ Hz, $J_{4,8} = 7.0$ Hz, H-4), 3.68-3.50 (m, 4H, OCH_2CH_2Cl), 2.33 (ddd, 1H, $J_{1,6endo} = 1.5$ Hz, $J_{5,6endo} = 8.9$ Hz, $J_{6exo,6endo} = 14.1$ Hz, H-6_{endo}), 2.05 (dt, 1H, $J_{1,6exo} = J_{5,6exo} = 3.4$ Hz, $J_{6exo,6endo} = 14.1$ Hz, H-6_{exo}); ^{13}C NMR **5-endo cycloadduct** 170.3 (C-3), 127.9 (C-8), 120.7 (C-7), 80.8 (C-1), 71.9 (C-5), 69.8 (OCH_2CH_2Cl), 48.8 (C-4), 43.0 (OCH_2CH_2Cl), 35.5 (C-6) **5-exo cycloadduct** 169.4 (C-3), 127.7 (C-8), 124.1 (C-7), 81.5 (C-1), 73.8 (C-5), 69.8 (OCH_2CH_2Cl), 48.6 (C-4), 42.8 (OCH_2CH_2Cl), 34.1 (C-6); IR 2926, 1766, 1617, 1460, 1432, 1357, 1302, 1276, 1167, 1115, 1033, 992, 918, 873, 842, 820, 802, 763, 737, 667, 650, 627, 542, 509, 490, 477, 469, 465 cm^{-1} ; m/z 283 (5), 282 (9, M^+), 281 (4), 280 (7, M^+), 203 (6), 201 (5), 176 (55, $M^+ - 106$, retro Diels-Alder), 174 (56, $M^+ - 106$, retro Diels-Alder), 147 (37), 145 (38), 108 (46), 107 (9), 106 (100, $M^+ - 175$, retro Diels-Alder), 95 (9, 175 - Br), 78 (18), 77 (30), 65 (22), 63 (32), 62 (11), 43 (39), 39 (17); HRMS calcd for $C_9H_{10}^{79}Br^{37}ClO_3Na$: 304.93646; found: 304.93586.

Cycloaddition of 5-Iodo-2(H)-pyran-2-one and (2-Chloroethyl) vinyl ether

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 5-iodo-2(H)-pyran-2-one **13** (48 mg, 0.216 mmol), (2-chloroethyl) vinyl ether (0.5 mL, 6.1 mmol, 28 equiv), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two cycloadducts. Pure sample of the *endo* and *exo* cycloadducts were obtained by silica gel chromatography, using 20% v/v ethyl acetate in petroleum ether, 65 mg, 92%.

7-Iodo-5_{endo}-(2-chloroethoxy)-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene and **7-Iodo-5_{exo}-(2-chloroethoxy)-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene** ¹H NMR 5-endo cycloadduct 6.76 (dd, 1H, $J_{1,8} = 1.7$ Hz, $J_{4,8} = 6.5$ Hz, H-8), 5.17 (dt, 1H, $J_{1,6endo} = 1.7$ Hz, $J_{1,6exo} = 3.8$ Hz, H-1), 4.01 (dm, 1H, $J_{5,6exo} = 7.8$ Hz, H-5), 3.84 (dd, 1H, $J_{4,5} = 3.2$ Hz, $J_{4,8} = 6.5$ Hz, H-4), 3.69 (m, 2H, OCH₂CH₂Cl), 3.57 (dd, 2H, $J = 5.6$ Hz, 11.1 Hz, OCH₂CH₂Cl), 2.51 (ddd, 1H, $J_{1,6exo} = 3.8$ Hz, $J_{5,6exo} = 7.8$ Hz, $J_{6exo,6endo} = 14.3$ Hz, H-6_{exo}), 1.76 (dm, 1H, $J_{6exo,6endo} = 14.3$ Hz, H-6_{endo}) 5-exo cycloadduct 6.76 (dd, 1H, $J_{1,8} = 1.9$ Hz, $J_{4,8} = 6.7$ Hz, H-8), 5.14 (m, 1H, H-1), 3.89 (dt, 1H, $J_{4,5} = 3.3$ Hz, $J_{5,6exo} = 3.3$ Hz, $J_{5,6endo} = 8.8$ Hz, H-5), 3.75 (dd, 1H, $J_{4,5} = 3.3$ Hz, $J_{4,8} = 6.7$ Hz, H-4), 3.68-3.60 (m, 4H, OCH₂CH₂Cl), 2.30 (ddd, 1H, $J_{1,6endo} = 1.5$ Hz, $J_{5,6endo} = 8.8$ Hz, $J_{6exo,6endo} = 14.1$ Hz, H-6_{endo}), 1.96 (dt, 1H, $J_{1,6exo} = 3.4$ Hz, $J_{6exo,6endo} = 14.1$ Hz, H-6_{exo}); ¹³C NMR 5-endo cycloadduct 170.1 (C-3), 136.5 (C-8), 90.6 (C-7), 83.7 (C-1), 71.9 (C-5), 69.8 (OCH₂CH₂Cl), 50.1 (C-4), 43.0 (OCH₂CH₂Cl), 34.9 (C-6) 5-exo cycloadduct 170.1 (C-3), 136.6 (C-8), 94.4 (C-7), 83.8 (C-1), 73.5 (C-5), 69.8 (OCH₂CH₂Cl), 49.9 (C-4), 42.8 (OCH₂CH₂Cl), 33.7 (C-6); IR 3076, 2956, 2924, 2863, 1761, 1684, 1601, 1460, 1430, 1355, 1301, 1260, 1169, 1113, 1025, 1008, 990, 917, 874, 800, 762, 738, 666, 638, 623 cm⁻¹; m/z 330 (10), 328 (27, M⁺), 223 (13), 222 [100, (M⁺-106, retro Diels-Alder)], 194 (33), 109(12), 108 (36), 107 (31), 106 [87, (M⁺-222, retro Diels-Alder)], 95 (10), 78 (17), 77 (8), 66 (7), 65 (11), 63 (29), 62 (6), 57 (6); HRMS calcd for C₉H₁₀³⁵ClIO₃Na: 350.92554; found: 350.92643.

Cycloaddition of 5-Chloro-2(H)-pyran-2-one and 1-Hexene

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 5-Chloro-2(H)-pyran-2-one **12** (35 mg, 0.27 mmol), 1-hexene (0.4 mL, 3.2 mmol, 12 equiv), dichloromethane (ca 0.5 mL), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-

polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 90 °C. After 4 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of three cycloadducts. Silica gel chromatography, using 10% v/v ethyl acetate in petroleum ether, afforded a mixed sample of 5-*endo* and 5-*exo* cycloadducts as well as samples of 6-*endo* and 6-*exo* cycloadducts contaminated with other cycloadducts.. Combined isolated yield of cycloadducts was 39 mg, 68%.

7-Chloro-5-*endo*-butyl-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene and **7-Chloro-5-*exo*-butyl-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene** ¹H NMR 5-*endo* cycloadduct 6.25 (dd, 1H, $J_{1,8} = 2.5$ Hz, $J_{4,8} = 6.7$ Hz, H-8), 5.00 (m, 1H, H-1), 3.49 (dd, 1H, $J_{4,5} = 2.4$ Hz, $J_{4,8} = 6.7$ Hz, H-4), 2.44 (ddd, 1H, $J_{1,6\text{exo}} = 4.2$ Hz, $J_{5,6\text{exo}} = 9.2$ Hz, $J_{6\text{exo},6\text{endo}} = 13.5$ Hz, H-6_{exo}), 2.11 (m, 1H, H-5), 1.39 (ddd, 1H, $J_{1,6\text{endo}} = 1.3$ Hz, $J_{5,6\text{endo}} = 4.1$ Hz, $J_{6\text{exo},6\text{endo}} = 13.5$ Hz, H-6_{endo}), 1.35-1.23 [m, 6H, -(CH₂)₃CH₃], 0.89 [t, 3H, $J = 6.8$ Hz, -(CH₂)₃CH₃]; 5-*exo* cycloadduct 6.39 (dd, 1H, $J_{1,8} = 2.5$ Hz, $J_{4,8} = 6.9$ Hz, H-8), 5.00 (m, 1H, H-1), 3.40 (dd, 1H, $J_{4,5} = 2.3$ Hz, $J_{4,8} = 6.9$ Hz, H-4), 2.10 (ddd, 1H, $J_{1,6\text{endo}} = 1.7$ Hz, $J_{5,6\text{endo}} = 10.0$ Hz, $J_{6\text{endo},6\text{exo}} = 13.4$ Hz, H-6_{endo}), 1.88 (m, 1H, H-5), 1.71 (dt, 1H, $J_{1,6\text{exo}} = J_{5,6\text{exo}} = 4.3$ Hz, $J_{6\text{endo},6\text{exo}} = 13.4$ Hz, H-6_{endo}), 1.35-1.20 [m, 6H, -(CH₂)₃CH₃], 0.89 [t, 3H, $J = 6.8$ Hz, -(CH₂)₃CH₃]; ¹³C NMR 5-*endo* cycloadduct 173.1 (C-3), 133.7 (C-7), 124.3 (C-8), 79.8 (C-1), 46.9 (C-4), 34.8 (C-6), 34.7 (C-5), 33.2 [CH₂(CH₂)₂CH₃], 29.7 (CH₂CH₂CH₂CH₃), 22.9 [(CH₂)₂CH₂CH₃], 14.3 [(CH₂)₃CH₃]; 5-*exo* cycloadduct 171.9 (C-3), 134.0 (C-7), 127.0 (C-8), 80.2 (C-1), 47.6 (C-4), 35.4 (C-6), 33.0 (C-5), 32.9 [CH₂(CH₂)₂CH₃], 30.2 (CHCH₂CH₂CH₂CH₃), 22.9 [(CH₂)₂CH₂CH₃], 14.3 [(CH₂)₃CH₃]; IR 2958,2928, 2857, 1767, 1625, 1466, 1358, 1276, 1198, 1164, 1143, 1056, 1005, 860, 797, 695, 641 cm⁻¹; m/z 217 (6, MH⁺ for ³⁷Cl), 215 (17, MH⁺ for ³⁵Cl), 172 [12, (M⁺ for ³⁷Cl-CO₂)], 170 [35, (M⁺ for

$^{35}\text{Cl-CO}_2$], 135 [16, ($\text{M}^+ - \text{CO}_2\text{-Cl}$)], 132 (30), 131 (24), 130 [90, ($\text{M}^+ - 84$, retro Diels-Alder)], 127 (17), 116 (20), 115 (48), 114 (71), 113 (100), 112 (44), 102 (28), 100 (10), 94 (21), 91 (21), 79 (26), 78 (15), 77 (100), 65 (12), 57 (25), 55 (12); HRMS calcd for $\text{C}_{11}\text{H}_{15}\text{ClO}_2\text{Na}$: 237.6805; found: 237.06494; Anal calcd for $\text{C}_{11}\text{H}_{15}\text{ClO}_2$: C, 61.54, H, 7.04; found: C, 61.60, H, 7.15.

7-Chloro-6_{endo}-butyl-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene $^1\text{H NMR}$ 6.40 (dd, 1H, $J_{1,8} = 2.4$ Hz, $J_{4,8} = 6.8$ Hz, H-8), 5.03 (t, 1H, $J_{1,8} = 2.4$ Hz, $J_{1,6} = 3.0$ Hz, H-1), 3.47 (dm, 1H, $J_{4,8} = 6.8$ Hz, H-4), 2.40 (m, 1H, H-6), 2.15 (ddd, 1H, $J_{4,5\text{exo}} = 3.1$ Hz, $J_{5\text{exo},6} = 9.4$ Hz, $J_{5\text{endo},5\text{exo}} = 12.8$ Hz, H-5_{exo}), 1.40-1.18 [m, 6H, $(\text{CH}_2)_3\text{CH}_3$], 1.13 (ddd, 1H, $J_{4,5\text{endo}} = 2.5$ Hz, $J_{5\text{endo},6} = 5.3$ Hz, $J_{5\text{endo},5\text{exo}} = 12.8$ Hz, H-5_{endo}), 0.91 [t, 3H, $J = 6.8$ Hz, $-(\text{CH}_2)_3\text{CH}_3$].

7-Chloro-6_{exo}-butyl-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene $^1\text{H NMR}$ 6.32 (dd, 1H, $J_{1,8} = 2.5$ Hz, $J_{4,8} = 6.7$ Hz, H-8), 4.85 (m, 1H, H-1), 3.48 (m, 1H, H-4), 2.00 (m, 1H, H-6), 1.91 (ddd, 1H, $J_{4,5\text{endo}} = 2.8$ Hz, $J_{5\text{endo},6} = 10.3$ Hz, $J_{5\text{endo},5\text{exo}} = 12.6$ Hz, H-5_{endo}), 1.46 (dt, 1H, $J_{4,5\text{exo}} = 3.0$ Hz, $J_{5\text{exo},6} = 3.0$ Hz, $J_{5\text{endo},5\text{exo}} = 12.6$ Hz, H-5_{exo}), 1.40 - 1.18 [m, 6H, $-(\text{CH}_2)_3\text{CH}_3$], 0.91 [t, 3H, $J = 6.8$ Hz, $-(\text{CH}_2)_3\text{CH}_3$].

Cycloaddition of 5-Bromo-2(H)-pyran-2-one and 1-Hexene

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 5-bromo-2(H)-pyran-2-one **5** (67 mg, 0.38 mmol), 1-hexene (0.6 mL, 4.8 mmol, 13 equiv), dichloromethane (ca 1 mL), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two cycloadducts and unreacted starting material (ca 5%). Silica gel chromatography, using 25% v/v ethyl acetate in petroleum ether, afforded a mixed sample of 5-*endo* and

5-*exo* cycloadducts as well as samples of 6-*endo* and 6-*exo* cycloadducts contaminated with other cycloadducts. Combined isolated yield of cycloadducts was 79 mg, 80%.

7-Bromo-5-*endo*-butyl-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene and **7-Bromo-5-*exo*-butyl-3-oxo-2-**

oxabicyclo[2.2.2]oct-7-ene ¹H NMR 5-*endo* cycloadduct 6.48 (dd, 1H, $J_{1,8} = 2.4$ Hz, $J_{4,8} = 6.7$ Hz, H-8), 5.07 (m, 1H, H-1), 3.49 (dd, 1H, $J_{4,5} = 2.4$ Hz, $J_{4,8} = 6.7$ Hz, H-4), 2.41 (ddd, 1H, $J_{1,6\text{exo}} = 4.2$ Hz, $J_{5,6\text{exo}} = 9.0$ Hz, $J_{6\text{exo},6\text{endo}} = 13.5$ Hz, H-6_{exo}), 2.10 (m, 1H, H-5), 1.39 (ddd, 1H, $J_{1,6\text{endo}} = 1.3$ Hz, $J_{5,6\text{endo}} = 4.0$ Hz, $J_{6\text{exo},6\text{endo}} = 13.5$ Hz, H-6_{endo}), 1.35 - 1.23 [m, 6H, -(CH₂)₃CH₃], 0.89 [t, 3H, J = 6.8 Hz, -(CH₂)₃CH₃]; 5-*exo* cycloadduct 6.61 (dd, 1H, $J_{1,8} = 2.5$ Hz, $J_{4,8} = 6.8$ Hz, H-8), 5.07 (m, 1H, H-1), 3.40 (dd, 1H, $J_{4,5} = 2.3$ Hz, $J_{4,8} = 6.8$ Hz, H-4), 2.09 (ddd, 1H, $J_{1,6\text{endo}} = 1.7$ Hz, $J_{5,6\text{endo}} = 10.0$ Hz, $J_{6\text{endo},6\text{exo}} = 13.5$ Hz, H-6_{endo}), 1.87 (m, 1H, H-5), 1.71 (dt, 1H, $J_{1,6\text{exo}} = J_{5,6\text{exo}} = 4.3$ Hz, $J_{6\text{endo},6\text{exo}} = 13.5$ Hz, H-6_{endo}), 1.35 - 1.23 [m, 6H, -(CH₂)₃CH₃], 0.89 [t, 3H, J = 6.8 Hz, -(CH₂)₃CH₃]; ¹³C NMR 5-*endo* cycloadduct 172.8 (C-3), 131.8 (C-7), 120.8 (C-8), 81.6 (C-1), 48.1 (C-4), 34.9 (C-6), 32.9 (C-5), 32.85 [CH₂(CH₂)₂CH₃], 29.7 (CHCH₂CH₂CH₂CH₃), 22.9 [(CH₂)₂CH₂CH₃], 14.3 [(CH₂)₃CH₃]; 5-*exo* cycloadduct 171.7 (C-3), 129.1 (C-7), 121.2 (C-8), 81.3 (C-1), 48.8 (C-4), 35.4 (C-6), 34.3 (C-5), 33.1 [CH₂(CH₂)₂CH₃], 30.2 (CH₂CH₂CH₂CH₃), 22.9 [(CH₂)₂CH₂CH₃], 14.3 [(CH₂)₃CH₃]; IR 2957, 2929, 2857, 1767, 1616, 1466, 1357, 1197, 1163, 1143, 1106, 1001, 975, 964, 861, 796, 646, 636, 529 cm⁻¹; m/z 261 (21, M⁺ for ⁸¹Br), 259 (21, M⁺ for ⁷⁹Br), 216 [39, (M⁺ for ⁸¹Br - CO₂)], 215 (11), 214 [39, (M⁺ for ⁷⁹Br - CO₂)], 176 [64, (M⁺ for ⁸¹Br - 84, retro Diels-Alder)], 175 (15), 174 [67, (M⁺ for ⁷⁹Br - 84, retro Diels-Alder)], 173 (11), 171 (12), 160 (50), 159 [100, (M⁺-CO₂-butyl)], 158 (84), 157 (99), 156 (37), 147 (21), 145 (27), 135 [37, (M⁺-CO₂-Br)], 94 (28), 93 (21), 92 (14), 91 (29), 79 (38), 78 (75), 77 (100), 65 (16), 57 (34); HRMS calcd for C₁₁H₁₅BrO₂Na: 282.1315; found: 283.01208 for C₁₁H₁₅⁸¹BrO₂Na and 282.01412 for C₁₁H₁₅⁷⁹BrO₂Na

7-Bromo-6_{endo}-butyl-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.63 (dd, 1H, $J_{1,8} = 2.4$ Hz, $J_{4,8} = 6.8$ Hz, H-8), 5.03 (t, 1H, $J_{1,8} = 2.4$ Hz, $J_{1,6} = 3.0$ Hz, H-1), 3.47 (dm, 1H, $J_{4,8} = 6.8$ Hz, H-4), 2.42 (m, 1H, H-6), 2.13 (ddd, 1H, $J_{4,5\text{exo}} = 3.1$ Hz, $J_{5\text{exo},6} = 9.3$ Hz, $J_{5\text{endo},5\text{exo}} = 12.8$ Hz, H-5_{exo}), 1.36-1.22 [m, 6H, (CH₂)₃CH₃], 1.14 (ddd, 1H, $J_{4,5\text{endo}} = 2.5$ Hz, $J_{5\text{endo},6} = 5.3$ Hz, $J_{5\text{endo},5\text{exo}} = 12.8$ Hz, H-5_{endo}), 0.91 [t, 3H, $J = 6.8$ Hz, (CH₂)₃CH₃].

7-Bromo-6_{exo}-butyl-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.53 (dd, 1H, $J_{1,8} = 2.4$ Hz, $J_{4,8} = 6.7$ Hz, H-8), 4.92 (m, 1H, H-1), 3.47 (dm, 1H, $J_{4,8} = 6.7$ Hz, H-4), 2.00 (m, 1H, H-6), 1.90 (ddd, 1H, $J_{4,5\text{endo}} = 2.8$ Hz, $J_{5\text{endo},6} = 10.2$ Hz, $J_{5\text{endo},5\text{exo}} = 12.8$ Hz, H-5_{endo}), 1.43 (dt, 1H, $J_{4,5\text{exo}} = 3.2$ Hz, $J_{5\text{exo},6} = 9.3$ Hz, H-5_{exo}), 1.45-1.18 [m, 6H, (CH₂)₃CH₃], 0.91 [t, 3H, $J = 6.8$ Hz, -(CH₂)₃CH₃].

Cycloaddition of 5-Iodo-2(H)-pyran-2-one and 1-Hexene

A sealed pressure tube (purchased from Aldrich Chemical Co. Cat No Z18,109-9) was charged with 5-iodo-2(H)-pyran-2-one **13** (34 mg, 0.153 mmol), 1-hexene (0.5 mL, mmol, equiv), dichloromethane (ca 1 mL), few crystals of 2,6-di-*tert*-butyl-4-methylphenol (acting as anti-polymerisation agent) and a small magnetic stirrer bar. The pressure tube was sealed and then immersed in an oil bath maintained at 100 °C. After 3 days, the tube was cooled to room temperature and the contents were stripped of volatile materials. Proton nuclear magnetic resonance of the crude residue indicated the presence of two cycloadducts and unreacted starting material (ca 15%). Silica gel chromatography, using 25% v/v ethyl acetate in petroleum ether, afforded a mixed sample of 5-*endo* and 5-*exo* cycloadducts as well as samples of 6-*endo* and 6-*exo* cycloadducts contaminated with other cycloadducts. Combined isolated yield of cycloadducts was 40 mg, 85%.

7-Iodo-5-_{endo}-butyl-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene and **7-Iodo-5-_{exo}-butyl-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene** ¹H NMR 5-*endo* cycloadduct 6.77 (dd, 1H, $J_{1,8} = 2.0$ Hz, $J_{4,8} = 6.5$ Hz,

H-8), 5.13 (m, 1H, H-1), 3.41 (dd, 1H, $J_{4,5} = 2.3$ Hz, $J_{4,8} = 6.5$ Hz, H-4), 2.32 (ddd, 1H, $J_{1,6_{\text{exo}}} = 4.3$ Hz, $J_{5,6_{\text{exo}}} = 9.0$ Hz, $J_{6_{\text{exo}},6_{\text{endo}}} = 13.5$ Hz, H-6_{exo}), 2.05 (m, 1H, H-5), 1.41 (dm, 1H, $J_{6_{\text{exo}},6_{\text{endo}}} = 13.5$ Hz, H-6_{endo}), 1.47 - 1.21 [m, 6H, $-(\text{CH}_2)_3\text{CH}_3$], 0.89 [t, 3H, $J = 6.2$ Hz, $-(\text{CH}_2)_3\text{CH}_3$] 5-exo cycloadduct

6.91 (dd, 1H, $J_{1,8} = 2.2$ Hz, $J_{4,8} = 6.7$ Hz, H-8), 5.13 (m, 1H, H-1), 3.41 (dd, 1H, $J_{4,5} = 2.2$ Hz, $J_{4,8} = 6.7$ Hz, H-4), 2.06 (ddd, 1H, $J_{1,6_{\text{endo}}} = 1.5$ Hz, $J_{5,6_{\text{endo}}} = 9.9$ Hz, $J_{6_{\text{exo}},6_{\text{endo}}} = 13.4$ Hz, H-6_{endo}), 1.82 (m, 1H, H-5), 1.60 (dm, 1H, $J_{6_{\text{exo}},6_{\text{endo}}} = 13.4$ Hz, H-6_{exo}), 1.47 - 1.21 [m, 6H, $-(\text{CH}_2)_3\text{CH}_3$], 0.89 [t, 3H, $J = 6.2$ Hz, $-(\text{CH}_2)_3\text{CH}_3$]; ¹³C NMR 5-endo cycloadduct ppm 172.7 (C-3), 138.1 (C-8), 90.9 (C-7), 84.2 (C-1), 49.4 (C-4), 35.0 (C-6), 32.8 (C-5), 32.6 [$\text{CH}_2(\text{CH}_2)_2\text{CH}_3$], 29.7 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 22.9 [$(\text{CH}_2)_2\text{CH}_2\text{CH}_3$], 14.4 [$(\text{CH}_2)_3\text{CH}_3$] 5-exo cycloadduct 171.5 (C-3), 140.7 (C-8), 91.2 (C-7), 84.5 (C-1), 50.1 (C-4), 35.3 (C-6), 34.1 (C-5), 32.4 [$\text{CH}_2(\text{CH}_2)_2\text{CH}_3$], 30.2 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 22.9 [$(\text{CH}_2)_2\text{CH}_2\text{CH}_3$], 14.3 [$(\text{CH}_2)_3\text{CH}_3$]; IR 2956, 2928, 2857, 1760, 1600, 1466, 1356, 1273, 1248, 1222, 1164, 1144, 1105, 995, 944, 908, 889, 862, 796, 727, 690, 675, 635 cm^{-1} ; m/z 307 (6), 306 (8, M⁺), 262 [38, (M⁺-CO₂)], 222 [31, (M⁺ - 84, retro Diels-Alder)], 206 (25), 205 (34), 204 (17), 194 (10), 135 [14, (M⁺-CO₂-I)], 94 (12), 93 (23), 92 (13), 91 (23), 79 (36), 78 (100), 77 (26), 65 (11), 57 (27), 55 (14);

Anal calcd for C₁₁H₁₅IO₂: C, 43.16, H, 4.94; found: C, 43.21, H, 4.80.

7-Iodo-6_{endo}-butyl-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.94 (dd, 1H, $J_{1,8} = 2.4$ Hz, $J_{4,8} = 6.6$ Hz, H-8), 5.11 (m, 1H, H-1), 3.41 (dm, 1H, $J_{4,8} = 6.6$ Hz, H-4), 2.45 (m, 1H, H-6), 2.12 (ddd, 1H, $J_{4,5_{\text{exo}}} = 3.1$ Hz, $J_{5_{\text{exo}},6} = 9.2$ Hz, $J_{5_{\text{exo}},5_{\text{endo}}} = 12.8$ Hz, H-5_{exo}), 1.38-1.19 [m, 6H, $(\text{CH}_2)_3\text{CH}_3$], 1.12 (ddd, 1H, $J_{4,5_{\text{endo}}} = 2.4$ Hz, $J_{5_{\text{endo}},6} = 5.4$ Hz, $J_{5_{\text{exo}},5_{\text{endo}}} = 12.8$ Hz, H-5_{endo}), 0.92 [t, 3H, $J = 6.8$ Hz, $(\text{CH}_2)_3\text{CH}_3$].

7-Iodo-6_{exo}-butyl-3-oxo-2-oxabicyclo[2.2.2]oct-7-ene ¹H NMR 6.82 (dd, 1H, $J_{1,8} = 2.2$ Hz, $J_{4,8} = 6.5$ Hz, H-8), 4.97 (m, 1H, H-1), 3.38 (dd, 1H, $J_{4,5_{\text{endo}}} = 2.8$ Hz, $J_{4,8} = 6.5$ Hz, H-4), 1.95 (m, 1H, H-6),

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1.86 (ddd, 1H, $J_{4,5_{\text{endo}}} = 2.8 \text{ Hz}$, $J_{5_{\text{endo}},6} = 10.2 \text{ Hz}$, $J_{5_{\text{exo}},5_{\text{endo}}} = 13.0 \text{ Hz}$, H-5_{endo}), 1.41 (dm, 1H, $J_{5_{\text{exo}},5_{\text{endo}}} = 13.0 \text{ Hz}$, H-5_{exo}), 1.38-1.16 [m, 6H, (CH₂)₃CH₃], 0.92 [t, 3H, J = 6.8 Hz, (CH₂)₃CH₃].

Appendix 1: Crystal data for the 5-*exo* cycloadduct of 5-bromo-2(H)-pyran-2-one and acrylonitrile.

Table 1.

Empirical formula	C8 H6 Br N O2
Formula weight	228.05
Temperature	293(2) K
Diffractometer, wavelength	Bruker P4, 1.54178 Å
Crystal system, space group	Orthorhombic, Pna2(1)
Unit cell dimensions	a = 12.265(4) Å = 90° b = 6.773(2) Å = 90° c = 10.069(4) Å = 90°
Volume, Z	836.4(5) Å ³ , 4
Density (calculated)	1.811 Mg/m ³
Absorption coefficient	6.362 mm ⁻¹
F(000)	448
Crystal colour / morphology	Colourless needles
Crystal size	0.43 x 0.05 x 0.03 mm ³
range for data collection	7.22 to 59.93°
Index ranges	-13<=h<=0, 0<=k<=7, 0<=l<=11
Reflns collected / unique	664 / 664 [R(int) = 0.0000]
Reflns observed [F>4 (F)]	502
Absorption correction	Empirical
Max. and min. transmission	0.7194 and 0.2678
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	664 / 1 / 110
Goodness-of-fit on F ²	1.064
Final R indices [F>4 (F)]	R1 = 0.0486, wR2 = 0.1320 R1+ = 0.0486, wR2+ = 0.1320 R1- = 0.0502, wR2- = 0.1350
R indices (all data)	R1 = 0.0661, wR2 = 0.1472
Absolute structure parameter	x+ = 0.0(2), x- = 1.1(2)
Extinction coefficient	0.0001(7)
Largest diff. peak, hole	0.330, -0.318 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.000

Table 2. Bond lengths [Å] and angles [°].

C(1)-C(7)	1.49(2)
C(1)-C(6)	1.51(2)
C(1)-C(2)	1.559(17)
C(2)-C(9)	1.45(2)
C(2)-C(3)	1.550(19)
C(3)-C(4)	1.503(19)
C(4)-O(8)	1.507(19)
C(4)-C(5)	1.510(19)
C(5)-C(6)	1.31(2)
C(5)-Br(5)	1.859(14)
C(7)-O(7)	1.237(18)
C(7)-O(8)	1.340(17)
C(9)-N(9)	1.20(2)
C(7)-C(1)-C(6)	108.2(11)
C(7)-C(1)-C(2)	106.0(11)
C(6)-C(1)-C(2)	106.7(11)
C(9)-C(2)-C(3)	112.5(13)
C(9)-C(2)-C(1)	112.1(12)
C(3)-C(2)-C(1)	107.4(10)
C(4)-C(3)-C(2)	109.5(11)
C(3)-C(4)-O(8)	106.9(12)
C(3)-C(4)-C(5)	108.2(12)
O(8)-C(4)-C(5)	106.4(11)
C(6)-C(5)-C(4)	114.3(13)
C(6)-C(5)-Br(5)	126.7(12)
C(4)-C(5)-Br(5)	118.8(10)
C(5)-C(6)-C(1)	112.7(13)
O(7)-C(7)-O(8)	117.9(13)
O(7)-C(7)-C(1)	127.7(13)
O(8)-C(7)-C(1)	114.4(12)
C(7)-O(8)-C(4)	112.1(10)
N(9)-C(9)-C(2)	176.9(16)

Symmetry transformations used to generate equivalent atoms:

Appendix 2: Crystal data for the 5-*endo* cycloadduct of 3-chloro-2(H)-pyran-2-one and acrylonitrile.

Table 1.

Empirical formula	C8 H6 Cl N O2
Formula weight	183.59
Temperature	183(2) K
Diffractometer, wavelength	Bruker P4, 0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 10.194(3) Å = 90° b = 6.968(8) Å = 103.92(2)° c = 11.746(4) Å = 90°
Volume, Z	809.8(10) Å ³ , 4
Density (calculated)	1.506 Mg/m ³
Absorption coefficient	0.424 mm ⁻¹
F(000)	376
Crystal colour / morphology	Colourless platy needles
Crystal size	0.90 x 0.50 x 0.03 mm ³
range for data collection	3.43 to 24.99°
Index ranges	0<=h<=12, 0<=k<=8, -13<=l<=13
Reflns collected / unique	1488 / 1407 [R(int) = 0.0515]
Reflns observed [F>4 (F)]	902
Absorption correction	Empirical
Max. and min. transmission	0.8646 and 0.5587
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1407 / 0 / 110
Goodness-of-fit on F ²	0.982
Final R indices [F>4 (F)]	R1 = 0.0633, wR2 = 0.1442
R indices (all data)	R1 = 0.1181, wR2 = 0.1640
Extinction coefficient	0.027(8)
Largest diff. peak, hole	0.587, -0.367 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.000

Table 2. Bond lengths [Å] and angles [°].

C(1)-C(6)	1.510(8)
C(1)-C(7)	1.520(8)
C(1)-C(2)	1.583(7)
C(1)-Cl(1)	1.832(6)
C(2)-C(9)	1.469(8)
C(2)-C(3)	1.542(8)
C(3)-C(4)	1.518(9)
C(4)-O(8)	1.458(7)
C(4)-C(5)	1.509(9)
C(5)-C(6)	1.318(10)
C(7)-O(7)	1.205(7)
C(7)-O(8)	1.330(7)
C(9)-N(9)	1.143(9)
C(6)-C(1)-C(7)	109.0(5)
C(6)-C(1)-C(2)	108.4(4)
C(7)-C(1)-C(2)	103.0(4)
C(6)-C(1)-Cl(1)	113.5(4)
C(7)-C(1)-Cl(1)	111.5(4)
C(2)-C(1)-Cl(1)	111.0(4)
C(9)-C(2)-C(3)	112.8(5)
C(9)-C(2)-C(1)	109.6(4)
C(3)-C(2)-C(1)	107.6(4)
C(4)-C(3)-C(2)	108.4(5)
O(8)-C(4)-C(5)	108.5(5)
O(8)-C(4)-C(3)	106.5(5)
C(5)-C(4)-C(3)	109.2(5)
C(6)-C(5)-C(4)	113.1(6)
C(5)-C(6)-C(1)	112.9(5)
O(7)-C(7)-O(8)	121.5(5)
O(7)-C(7)-C(1)	126.7(5)
O(8)-C(7)-C(1)	111.8(5)
C(7)-O(8)-C(4)	114.3(4)
N(9)-C(9)-C(2)	179.0(7)

Symmetry transformations used to generate equivalent atoms:

Appendix 3: Crystal data for the 5-*endo* cycloadduct of 3-chloro-2(H)-pyran-2-one and methyl acrylate.

Table 1.

Empirical formula	C ₉ H ₉ Cl O ₄
Formula weight	216.61
Temperature	293(2) K
Diffractometer, wavelength	Bruker P4, 1.54178 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 13.061(4) Å = 90° b = 10.626(3) Å = 90° c = 13.427(3) Å = 90°
Volume, Z	1863.4(9) Å ³ , 8
Density (calculated)	1.544 Mg/m ³
Absorption coefficient	3.551 mm ⁻¹
F(000)	896
Crystal colour / morphology	Colourless blocks
Crystal size	0.40 x 0.20 x 0.12 mm ³
range for data collection	6.30 to 60.08°
Index ranges	0 ≤ h ≤ 14, 0 ≤ k ≤ 11, -15 ≤ l ≤ 0
Reflns collected / unique	1368 / 1368 [R(int) = 0.0000]
Reflns observed [F > 4 (F)]	909
Absorption correction	Empirical
Max. and min. transmission	0.5639 and 0.1011
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1368 / 0 / 128
Goodness-of-fit on F ²	1.606
Final R indices [F > 4 (F)]	R1 = 0.0920, wR2 = 0.2565
R indices (all data)	R1 = 0.1190, wR2 = 0.2808
Extinction coefficient	0.0053(13)
Largest diff. peak, hole	0.368, -0.317 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.000

Table 2. Bond lengths [Å] and angles [°].

C(1)-C(6)	1.517(11)
C(1)-C(7)	1.538(11)
C(1)-C(2)	1.568(10)
C(1)-Cl(1)	1.776(8)
C(2)-C(9)	1.511(11)
C(2)-C(3)	1.572(10)
C(3)-C(4)	1.518(11)
C(4)-O(8)	1.477(10)
C(4)-C(5)	1.486(12)
C(5)-C(6)	1.326(11)
C(7)-O(7)	1.193(9)
C(7)-O(8)	1.346(9)
C(9)-O(9)	1.192(10)
C(9)-O(10)	1.353(9)
O(10)-C(11)	1.460(9)

C(6)-C(1)-C(7)	105.4(7)
C(6)-C(1)-C(2)	109.4(6)
C(7)-C(1)-C(2)	105.0(6)
C(6)-C(1)-Cl(1)	114.0(5)
C(7)-C(1)-Cl(1)	110.9(5)
C(2)-C(1)-Cl(1)	111.6(5)
C(9)-C(2)-C(1)	111.5(6)
C(9)-C(2)-C(3)	109.6(6)
C(1)-C(2)-C(3)	107.8(6)
C(4)-C(3)-C(2)	107.8(6)
O(8)-C(4)-C(5)	108.0(7)
O(8)-C(4)-C(3)	107.1(7)
C(5)-C(4)-C(3)	110.2(7)
C(6)-C(5)-C(4)	113.6(8)
C(5)-C(6)-C(1)	113.1(8)
O(7)-C(7)-O(8)	121.9(8)
O(7)-C(7)-C(1)	126.0(8)
O(8)-C(7)-C(1)	112.1(7)
C(7)-O(8)-C(4)	113.5(6)
O(9)-C(9)-O(10)	125.6(8)
O(9)-C(9)-C(2)	127.7(7)
O(10)-C(9)-C(2)	106.8(7)
C(9)-O(10)-C(11)	114.2(7)

Symmetry transformations used to generate equivalent atoms:

Appendix 4: Crystal data for the 5-*endo* cycloadduct of 4-iodo-2(H)-pyran-2-one and methyl acrylate.

Table 1.

Empirical formula	C ₉ H ₉ I O ₄
Formula weight	308.06
Temperature	203(2) K
Diffractometer, wavelength	Bruker P4, 0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 10.3339(17) Å = 90° b = 9.4635(17) Å = 90° c = 20.543(3) Å = 90°
Volume, Z	2009.0(6) Å ³ , 8
Density (calculated)	2.037 Mg/m ³
Absorption coefficient	3.173 mm ⁻¹
F(000)	1184
Crystal colour / morphology	Colourless blocks
Crystal size	0.47 x 0.40 x 0.27 mm ³
range for data collection	2.80 to 24.99°
Index ranges	0 ≤ h ≤ 12, 0 ≤ k ≤ 11, -24 ≤ l ≤ 0
Reflns collected / unique	1775 / 1775 [R(int) = 0.0000]
Reflns observed [F > 4 (F)]	1315
Absorption correction	Ellipsoidal
Max. and min. transmission	0.3060 and 0.2107
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1775 / 0 / 128
Goodness-of-fit on F ²	1.001
Final R indices [F > 4 (F)]	R1 = 0.0387, wR2 = 0.0834
R indices (all data)	R1 = 0.0595, wR2 = 0.0905
Extinction coefficient	0.0009(2)
Largest diff. peak, hole	0.789, -0.583 eÅ ⁻³
Mean and maximum shift/error	0.000 and 0.001

Table 2. Bond lengths [Å] and angles [°].

C(1)-C(7)	1.515(8)
C(1)-C(6)	1.525(7)
C(1)-C(2)	1.572(7)
C(2)-C(3)	1.511(8)
C(2)-C(9)	1.517(8)
C(3)-C(4)	1.537(9)
C(4)-O(8)	1.469(7)
C(4)-C(5)	1.490(8)
C(5)-C(6)	1.320(9)
C(6)-I(6)	2.079(6)
C(7)-O(7)	1.209(7)
C(7)-O(8)	1.343(7)
C(9)-O(9)	1.198(7)
C(9)-O(10)	1.334(7)
O(10)-C(11)	1.447(8)

C(7)-C(1)-C(6)	106.9(5)
C(7)-C(1)-C(2)	105.7(4)
C(6)-C(1)-C(2)	106.3(4)
C(3)-C(2)-C(9)	114.4(5)
C(3)-C(2)-C(1)	108.7(5)
C(9)-C(2)-C(1)	108.4(4)
C(2)-C(3)-C(4)	108.6(5)
O(8)-C(4)-C(5)	108.7(5)
O(8)-C(4)-C(3)	107.1(4)
C(5)-C(4)-C(3)	108.8(5)
C(6)-C(5)-C(4)	113.1(5)
C(5)-C(6)-C(1)	113.2(5)
C(5)-C(6)-I(6)	124.6(4)
C(1)-C(6)-I(6)	122.2(4)
O(7)-C(7)-O(8)	121.4(6)
O(7)-C(7)-C(1)	125.4(6)
O(8)-C(7)-C(1)	113.3(5)
C(7)-O(8)-C(4)	112.6(5)
O(9)-C(9)-O(10)	123.9(6)
O(9)-C(9)-C(2)	125.9(6)
O(10)-C(9)-C(2)	110.2(5)
C(9)-O(10)-C(11)	116.5(5)

Symmetry transformations used to generate equivalent atoms:

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