Exploiting the Curtin-Hammett Principle – Recognition-Mediated Acceleration of an Aldol Reaction

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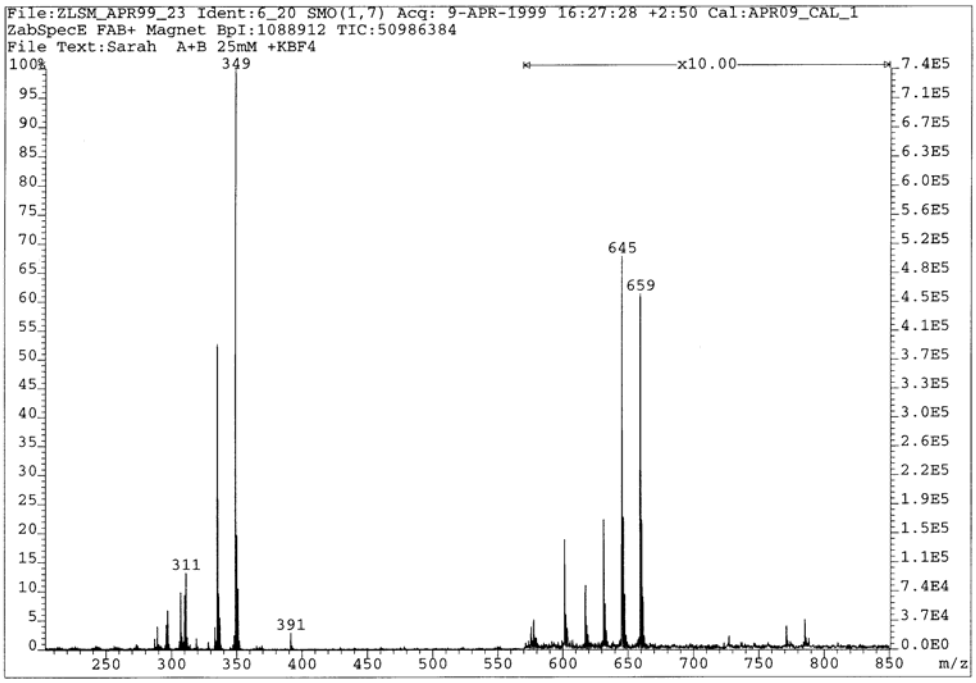
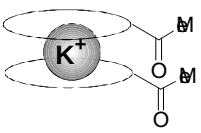
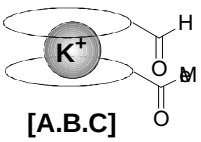
SUPPORTING INFORMATION

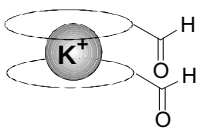
FABMS evidence for the formation of homo and mixed bis crown sandwich complexes in the presence of K^+



m/z 659 = 

m/z 645 = 

[A.B.C]

m/z 631 = 

4-Formylbenzo-15-crown-5 1

White solid (5.40 g, 23 %). Mp 79-81°C; (Found: C, 61.02; H, 6.90, $C_{15}H_{20}O_6$ requires C, 60.81; H, 6.81); ν_{max}/cm^{-1} 1690 (C=O), 1599, 1587 and 1511 (Ar, C=C); δ_H (300 MHz, $CDCl_3$) 7.42-7.39 (1H, dd, Ar, $^3J_{HH}$ 8.3, $^4J_{HH}$ 1.8), 7.35-7.34 (1H, d, Ar, $^4J_{HH}$ 1.8), 6.92-6.89 (1H, d, Ar, $^3J_{HH}$ 8.3), 4.18-4.14 (4H, m, 2 x CH_2), 3.92-3.87 (4H, m, 2 x CH_2), 3.74 (8H, s, 4 x CH_2); δ_C (75 MHz, $CDCl_3$); 191.0 (CHO), 154.6 (C, quat, Ar), 149.4 (C, quat, Ar), 130.2 (C, quat, Ar), 127.0 (CH, Ar), 111.9 (CH, Ar), 111.1 (CH, Ar), 71.2 (2 x CH_2), 70.3 (CH_2), 70.2 (CH_2), 69.3 (CH_2), 69.2 (CH_2), 68.7 (CH_2), 68.6 (CH_2); *m/z* (EIMS) 296 (M^+, 41%), 164 (100), 149 (51), 45 (41).

4-Acetylbenzo-15-crown-5 2

White solid (2.00 g, 58%). Mp 93-95°C; (Found; C, 61.93, H; 6.93, $C_9H_{11}N_3O_2$ requires C, 61.94; H, 7.10); ν_{max}/cm^{-1} 1668 ($COCH_3$), 1595 and 1518 (Ar, C=C) δ_H (300 MHz, $CDCl_3$); 7.56-7.52 (1H, dd, Ar, $^3J_{HH}$ 8.2, $^4J_{HH}$ 2.2), 7.49-7.48 (1H, d, Ar, $^4J_{HH}$ 2.2), 6.85-6.82 (1H, d, Ar, $^3J_{HH}$ 8.2), 4.18-4.16 (4H, m, 2 x CH_2), 3.93-3.74 (4H, m, 2 x CH_2), 3.74 (8H, s, 4 x CH_2), 2.53 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$); 178.2 (C=O), 134.8 (C, quat, Ar), 130.2 (C, quat, Ar), 112.0 (C, quat, Ar), 105.0 (CH, Ar), 93.9 (CH, Ar), 93.0 (CH, Ar), 52.5 (2 x CH_2), 51.7 (CH_2), 51.7 (CH_2), 50.7 (CH_2), 50.6 (CH_2), 50.3 (CH_2), 50.0 (CH_2), 26.4 (CH_3)**;** *m/z* (EIMS) 310 (M^+, 18%), 163 (89), 43 (100).

1,3-Bis-(3,4-benzo-15-crown-5)-propenone 3

Pale yellow oil (0.26 g, 56%); δ_H (300 MHz, $CDCl_3$) 7.72-7.67 (1H, d, alkene, $^3J_{HH}$ 15.4), 7.65-7.61 (1H, dd, Ar, $^3J_{HH}$ 8.4, $^4J_{HH}$ 1.8), 7.57-7.56 (1H, d, Ar, $^4J_{HH}$ 1.8), 7.38-7.33 (1H, d, alkene, $^3J_{HH}$ 15.4), 7.21-7.17 (1H, dd, Ar, $^3J_{HH}$ 8.3, $^4J_{HH}$ 1.8), 7.14-7.13 (1H, d, Ar, $^4J_{HH}$ 1.8), 6.88-6.83 (2H, dd, Ar, $^3J_{HH}$ 8.3, $^3J_{HH}$ 8.4), 4.22-4.13 (8H, m, 2 x CH_2), 3.93-3.89 (8H, m, 4 x CH_2), 3.74 (16H, s, 8 x CH_2); δ_C (75 MHz, $CDCl_3$) 188.7 (C, quat, C=O), 153.3 (C, 2 x quat, Ar), 151.5 (C, 2 x quat, Ar), 149.1 (C, quat, Ar), 149.0 (C, quat, Ar), 144.1 (CH, alkene, Ar), 123.4 (CH, alkene), 123.3 (2 x CH, Ar), 119.7 (CH, Ar), 113.3 (CH, Ar), 113.1 (CH, Ar), 113.0 (CH, Ar), 111.7 (CH, Ar), 71.1 (2 x CH_2), 71.0 (2 x CH_2), 70.4 (CH_2), 70.4 (CH_2), 70.3 (CH_2), 70.3 (CH_2), 69.5 (CH_2), 69.4 (CH_2), 69.3 (CH_2), 69.2 (CH_2), 69.2 (CH_2), 69.0 (CH_2), 68.6 (CH_2), 68.6 (CH_2); *m/z* (EI +70eV) 588 (M^+, 100%), 446 (62), 163 (60), 44 (78); (HRMS) 611.2468 ($M^+ C_{31}H_{40}O_{11}Na$) requires 611.2468).

4-Formylbenzo-18-crown-6 6

White solid (1.51 g, 27%); Mp 72-74°C; δ_H (300 MHz, $CDCl_3$) 9.82 (1H, s, CHO), 7.44-7.39 (1H, dd, Ar, $^3J_{HH}$ 8.1, $^4J_{HH}$ 1.8), 7.38-7.37 (1H, d, Ar, $^4J_{HH}$ 1.8), 6.96-6.93 (1H, d, Ar, $^3J_{HH}$ 8.1), 4.24-4.19 (4H, m, 2 x CH_2), 3.97-3.91 (4H, m, 2 x CH_2), 3.78-3.68 (12H, m, 6 x CH_2); δ_C (75 MHz, $CDCl_3$); 191.1 (CH, Ar), 154.6 (C, quat, C=O), 149.4 (C, quat, Ar), 130.3 (C, quat, Ar), 127.0 (CH, Ar), 112.1 (CH, Ar), 111.2 (CH, Ar), 71.1 (CH_2), 71.9 (CH_2), 70.9 (CH_2), 70.8 (CH_2), 70.7 (CH_2), 70.7 (CH_2), 69.5

(CH_2), 69.4 (CH_2), 69.1 (CH_2), 69.0 (CH_2); *m/z* (EIMS) 340 (M^+, 49%), 164 (82), 149 (68), 43 (100), 32 (49); (HRMS) 340.1517 (M^+ $C_{17}H_{24}O_7$) requires 340.1522).

4–Acetylbenzo-18-crown-6 7

White solid (1.0 g, 45%); Mp 78.5-79°C; δ_H (300 MHz, $CDCl_3$) 7.55-7.54 (1H, dd, Ar, $^3J_{HH}$ 8.3, $^4J_{HH}$ 1.8), 7.49-7.48 (1H, d, Ar, $^4J_{HH}$ 1.8), 6.86-6.83 (1H, d, Ar, $^3J_{HH}$ 8.3), 4.22-4.19 (4H, m, 2 x CH_2), 3.95-3.89 (4H, m, 2 x CH_2), 3.76-3.67 (12H, m, 6 x CH_2), 2.54 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$); 196.9 (C, quat, C=O), 153.3 (C, quat, Ar), 148.7 (C, quat, Ar), 130.6 (C, quat, Ar), 123.5 (CH, Ar), 112.6 (CH, Ar), 111.8 (CH, Ar), 71.0 (2 x CH_2), 70.9 (CH_2), 70.8 (CH_2), 70.7 (CH_2), 70.6 (CH_2), 69.5 (CH_2), 69.4 (CH_2), 69.1(CH_2), 68.9 (CH_2), 26.3 (CH_3)**;** *m/z* (ES) 377 ($[M + Na]^+$, 100%).