Supplementary materials

Preparation of benzo- and polybenzocrown ethers by macrocyclization reactions

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Table of contents

The following benzocrown and substituted benzocrown ethers were prepared using the general procedure for cesium-assisted cyclizations given in the Experimental Section of the paper.

Benzo-12-crown-4 (1) was obtained as a white solid with mp 44.5-45.5 °C (lit.[1] mp 44-45.5 °C) in 54% yield after recrystallization from hexanes. Mass spectroscopy revealed that the recrystallized product did not contain any [2+2] adduct. IR (deposit from a CDCl$_3$ solution onto a NaCl plate): 1260, 1142, 1124 and 1077 (C-O) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ3.74 (s, 4H); 3.78-3.96 (m, 4H); 4.10-4.16 (m, 4H); 6.86-6.99 (m, 4H).

4-*t*-Butylbenzo-12-crown-4 (2), a white solid, was isolated in 70% yield and contained 10-20% of the [2+2] adduct as estimated by ^{1}H NMR and mass spectroscopy. A small sample was recrystallized from hexanes for elemental analysis and the [1+1] adduct was obtained with mp 47-49 °C. Reaction products from several runs (4.10 g) were combined and purified by Kugelrohr distillation (130 °C/0.8 Torr) and the [1+1] adduct (1.10 g, 29%) was obtained with a mp of 47-49 °C. IR (deposit from a CDCl$_3$ solution onto a NaCl plate): 1237, 1122 and 1049 (C-O) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ1.26 (s, 9H); 3.79 (s, 4H); 3.80-3.86 (m, 4H); 4.11-4.20 (m, 4H); 6.85-6.99 (m, 3H). Anal. calcd for $C_{16}H_{24}O_4$: C, 68.55; H, 8.63. Found: C, 68.50; H, 8.59. MS (DIP-EI) *m/e* 280.30 (280.17 calculated for $C_{16}H_{24}O_4$) and 560.45 (560.34 calculated for $C_{32}H_{48}O_8$).

3,5-Di-*t*-Butylbenzo-12-crown-4 (3) was obtained as a white solid in 82% yield and contained ~50% of the [2+2] adduct as estimated from the ^{1}H NMR and mass spectra. Reaction products from several runs (2.02 g) were combined and purified by Kugelrohr distillation (140° C/0.8 Torr) and the [1+1] adduct (1.10 g, 54%) was obtained with mp 147-149 °C. Although the product could be recrystallized from hexanes, Kugelrohr distillation was found to be the superior method of isolating the pure [1+1] adduct. IR (deposit from a CDCl$_3$ solution onto a NaCl plate): 1235, 1135 and 1069 (C-O) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ1.26 (s, 9H); 1.35 (s, 9H); 3.80 (d, 7.4 Hz, 4H); 3.83-3.93 (m, 4H); 4.10-4.14 (m, 2H); 4.24 (t, 5.4 Hz, 2H); 6.76 (d, 2.2 Hz, 1H); 6.90 (d, 2.2 Hz, 1H). Anal. calcd for $C_{20}H_{32}O_4$: C, 71.39; H, 9.59. Found: C, 71.40; H, 9.54. MS (DIP-EI) *m/e* 336.40 (336.23 calculated for $C_{20}H_{32}O_4$); [2+2] *m/e* exceeds the detection limit.

Benzo-15-crown-5 (4) was isolated as a white solid in 69% yield and contained 10-20% of the [2+2] adduct as estimated from the ^{1}H NMR and mass spectra. The reaction products from several runs (1.52 g) were combined and recrystallized from heptane. The [1+1] adduct was isolated (1.10 g, 72%) with mp 77.5-79 °C (lit.[1] mp 79-79.5 °C). IR (deposit from a CDCl$_3$ solution onto a NaCl plate): 1230, 1121 and 1075 (C-O) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ3.88 (s, 8H); 3.90-3.93 (m, 4H); 4.10-4.16 (m, 4H); 6.64-6.94 (m, 4H). *m/e* 268.20 (268.13 calculated for $C_{14}H_{20}O_5$) and 536.40 (536.26 calculated for $C_{32}H_{48}O_8$).

4-*t*-Butylbenzo-15-crown-5 (5) was obtained as a colorless oil (71%) after Kugelrohr distillation and identified by its ^{1}H NMR and mass spectra as the [1+1] product. After crystallization from diethyl ether at 0 °C, the [1+1] adduct had mp 42-44 °C (lit.[1] mp below 26 °C). IR (deposit from a CDCl$_3$ solution onto a NaCl plate): 1264 and 1141 (C-O) cm^{-1}. ^{1}H NMR (200 MHz, CDCl$_3$): δ

1.26 (s, 9H); 3.73 (s, 8H); 3.84-3.92 (m, 4H); 4.08-4.16 (m, 4H); 6.79-6.90 (m, 3H). MS (DIP-EI) *m/e* 324.25 (324.19 calculated for $C_{18}H_{28}O_5$) and 648.35 (648.38 calculated for $C_{36}H_{56}O_8$).

3,5-Di-*t*-Butylbenzo-15-crown-5 (6) was a white crystalline solid formed in 87% yield and contained 10-20% of the [2+2] adduct as estimated by the ^{1}H NMR and mass spectra. Reaction products from several runs were combined (3.02 g, 82%) and recrystallized from heptane and the [1+1] product was isolated with mp of 99.5-100.5 ^{o}C. IR (deposit from a $CDCl_3$ solution onto a NaCl plate): 1234, 1133 and 1073 (C-O) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.26 (s, 9H); 1.35 (s, 9H); 3.72-3.80 (m, 8H); 3.87-3.91 (m, 2H); 4.02 (t, 4.0 Hz, 2H); 4.10-4.12 (m, 2H); 4.26 (t, 4.0 Hz, 2H); 6.76 (d, 2.2 Hz, 1H); 6.89 (d, 2.2 Hz, 1H). Anal. calcd for $C_{22}H_{36}O_5$: C, 69.44; H, 9.53. Found: C, 69.84; H, 9.70. MS (DIP-EI) *m/e* 380.40 (380.26 calculated for $C_{22}H_{36}O_5$) and 760.70 (760.52 calculated for $C_{44}H_{72}O_{10}$).

4-*t*-Butylbenzo-18-crown-6 (7) was a yellow oil obtained in 72% yield and contained 10-20% of the [2+2] adduct as shown by the ^{1}H NMR and mass spectra. Reaction products from several runs (4.55 g) were combined then purified by Kugelrohr distillation (180° C, 0.8 Torr) and the [1+1] adduct (4.31 g, 95%) was obtained. Upon standing over a period of several months, the yellow oil spontaneously crystallized resulting in a white solid identified as the [1+1] adduct with mp 34-36 ^{o}C (lit.[1] mp below 26 ^{o}C). IR (deposit from a $CDCl_3$ solution onto a NaCl plate): 1266 and 1136 (C-O) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.26 (s, 9H); 3.64-3.77 (m, 12H); 3.86-3.93 (m, 4H); 4.09-4.16 (m, 4H); 6.76-6.92 (m, 3H). MS (DIP-EI) *m/e* 368.30 (368.22 calculated for $C_{20}H_{32}O_6$) and 736.40 (736.60 calculated for $C_{16}H_{24}O_4$).

3,5-Di-*t*-Butylbenzo-18-crown-6 (8) was a yellow oil obtained in 82% yield and contained 10-20% of the [2+2] adduct as shown by the ^{1}H NMR and mass spectra. Reaction products from several runs (6.43 g) were combined then purified by Kugelrohr distillation (190° C/0.8 Torr) and the [1+1] adduct (3.97 g, 62%) was obtained. IR (deposit from a $CDCl_3$ solution onto a NaCl plate): 1234, 1129 and 1073 (C-O) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.26 (s, 9H); 1.35 (s, 9H); 3.66-3.76 (m, 12H); 3.89-3.96 (m, 4H) 3.89-3.96 (m, 4H); 4.11 (t, 5.4 Hz, 2H); 4.24 (t, 5.4 Hz, 2H); 6.78 (d, 2.2 Hz, 1H); 6.6.90 (d, 2.2 Hz, 1H). Anal. calcd for $C_{24}H_{40}O_6$: C, 67.89; H, 9.50. Found: C, 68.04; H, 9.36. MS (DIP-EI) *m/e* 424.30 (424.28 calculated for $C_{24}H_{40}O_6$); [2+2] *m/e* exceeds detection limit.

4-*t*-Butylbenzo-21-crown-7(9) was a yellow oil obtained in 78% yield and contained 10-20% of the [2+2] adduct as estimated by the ^{1}H NMR and mass spectra. Reaction products from several runs (~ 23 g) were combined then purified by Kugelrohr distillation (190° C/0.8 Torr) and the [1+1] adduct was obtained. The product (13.11 g, 57%) combined after 3 Kugelrohr distillations was identified as the desired [1+1] adduct by the ^{1}H NMR and mass spectra. IR (deposit from a $CDCl_3$ solution onto a NaCl plate): 1266 and 1128 (C-O) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.26 (s, 9H); 3.62-3.78 (m, 16H); 3.85-3.92 (m, 4H); 4.09-4.17 (m, 4H); 6.79-6.90 (m, 3H). MS (DIP-EI) *m/e* 412.30 (412.25 calculated for $C_{22}H_{36}O_7$); [2+2] *m/e* exceeds detection limit.

3,5-Di-*t*-Butylbenzo-21-crown-7 (10) was a yellow oil obtained in 78% yield and contained 10-20% of the [2+2] adduct as estimated by the ^{1}H NMR and mass spectra. Reaction products from several runs (6.21 g) were combined and purified by Kugelrohr distillation (190 °C/0.8 Torr) and the [1+1] adduct (1.00 g, 16%) was obtained. IR (deposit from a $CDCl_3$ solution onto a NaCl plate): 1234, 1126 and 1071 (C-O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 1.26 (s, 9H); 1.35 (s, 9H); 3.65-3.73 (m, 16H); 3.86-3.95 (m, 4H); 4.12 (t, 5.0 Hz, 2H); 4.24 (t, 5.0 Hz, 2H); 6.77 (d, 2.2 Hz, 1H); 6.90 (d, 2.2 Hz, 1H). Anal. calcd for $C_{26}H_{44}O_7$: C, 66.64; H, 9.46. Found: C, 66.91; H, 9.56. MS (DIP-EI) *m/e* 424.25 (424.28 calculated for $C_{26}H_{44}O_7$); [2+2] *m/e* exceeds detection limit.

References

1. Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.