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Synthesis of 5,6-indolo-12-crown-4 ethers

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o-Alkyl derivatives of *N*-acetylaminobenzo-12-crowns-4 **4a—f** were prepared by Pd—Cu-catalyzed alkynylation of 5´-*N*-acetylamino-4´-iodobenzo-12-crown-4 (**2**). Cyclization of compounds **4a—f** afforded the corresponding substituted 5,6-indolo-12-crowns-4 **5a—c**.

Key words: cross-coupling, benzocrown ethers, acetylenic derivatives, *N*-acetylamines, cyclization, indolocrown ethers.

Benzocrown ethers attract attention of researchers because of their ability to bind cations with high specificity.[1] It is known that the functional group in the benzene ring influences the complex formation and allows the preparation of polymeric and immobilized crown compounds. In this connection, the synthesis and properties of functionally substituted crown ethers are being studied intensively. Derivatives of benzocrown ethers are widely used in organic synthesis[2] and analytical chemistry.[3] The important field of application of crown compounds is based on the fact that they can readily penetrate through biological membranes.[2] If a molecule, which is a component of pharmaceuticals or pesticides, is covalently bound to a crown ether, its transport through a cell membrane becomes much easier.[2] Among these molecules are, undoubtedly, indole derivatives, which occur in nature[4] and exhibit various biological activities.[5,6]

In the present study, we synthesized substituted 5,6-indole-12-crowns-4 by cyclization of *o*-alkynyl derivatives of 4´-*N*-acetylaminobenzo-12-crown-4. This type of cyclization was reported for *o*-alkynylanilines[7—13] and amides of *vic*-alkynylpyrazolecarboxylic acids.[14] In addition, the possibility of this reaction being performed for benzocrown ethers has not been evident because the electron-donating alkoxy groups exert a passivating effect on the electrophilicity of the triple bond (+M effect).

Results and Discussion

Since attempts to carry out efficient iodination of 4´-aminobenzo-12-crown-4 under various conditions (I_2, KI, Na_2CO_3 in H_2O; I_2 in DMSO; I_2, HIO_3, H_2SO_4 in AcOH) failed, we used 4´-*N*-acetylaminobenzo-12-crown-4 (**1**) as the starting compound in the synthesis. The reaction of the latter with I_2 and HIO_3 in a mixture of dilute H_2SO_4 and acetic acid (*cf*. lit. data[15]) at 65 °C was completed in 10 h to form 5´-*N*-acetylamino-4´-iodobenzo-12-crown-4 (**2**) in 65% yield.

Condensation of iodide **2** with alkynes **3a—c,e** was carried out in benzene in the presence of $PhPdI(PPh_3)_2$, CuI, and NEt_3 at 70—75 °C under argon.[16] The reaction was completed in 20—40 min to give ethers **4a—c,e** in 40—80% yields. These reaction conditions proved to be inefficient in the case of cross-coupling of iodide **2** with *p*-ethynylbenzaldehyde (**3d**). In the course of the latter reaction, a finely dispersed black precipitate was obtained, which was apparently palladium metal formed due to decomposition of its complex.

Previously,[17] cross-coupling of isomeric bromobenzaldehydes with trimethylsilylacetylene has been carried out in the presence of catalytic amounts of $Pd(OAc)_2$ and PPh_3; however, iodide **2** did not react with alkyne **3d** under these conditions. It is known[18] that activation of the alkynyl component by adding CuI leads to a substantial acceleration of cross-coupling of aryl halides with terminal acetylenes. We found that the reaction of compound **2** with **3d** in the system involving $Pd(OAc)_2$, PPh_3, and NEt_3 in the presence of CuI afforded ether **4d** in 60% yield. Ethynyl derivative **4f** was prepared from compound **4e** by removing the trimethylsilyl group under the action of K_2CO_3 (Scheme 1).

Indole was first synthesized[19] by thermal cyclization of *o*-ethynylaniline at 600 °C. Shortly thereafter, it was found that CuCl-catalyzed cyclization of *o*-ethynylaniline proceeded even at 170—180 °C.[20] Later on, the reaction of this type was carried out in the presence of CuI in DMF,[8,10] CuI and $CaCO_3$ in DMF,[9] CuC≡CPh in DMF,[7] and $PdCl_2$ in MeCN.[11—13] If the substituent R exhibits electron-withdrawing properties, *o*-alkynylaniline derivatives can be subjected to cyclization under the actions of bases, for example, of NaOEt.[21]

Cyclization of *N*-acetylaminophenylalkynes **4a—f** was carried out under the action of KOH in EtOH by analogy

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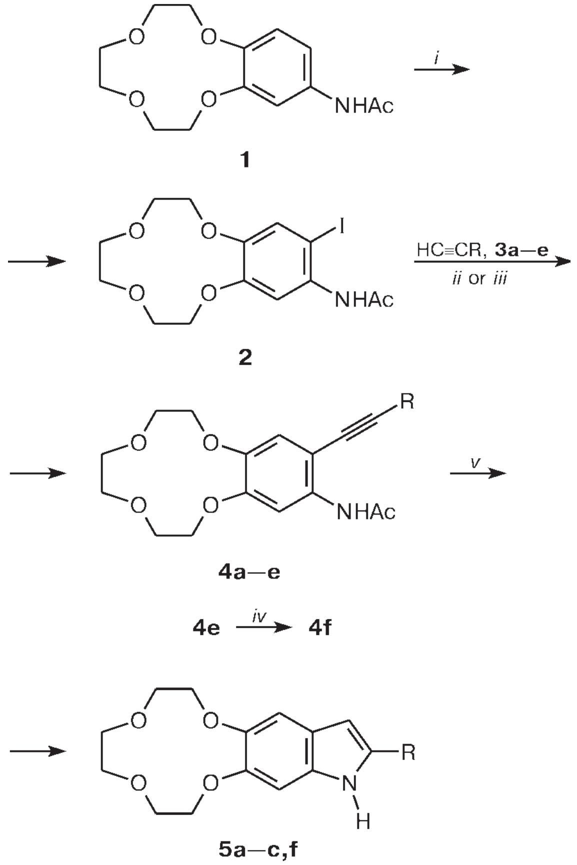
Scheme 1



R = Ph (**a**); 4-MeOC$_6$H$_4$ (**b**); 4-O$_2$NC$_6$H$_4$ (**c**); 4-(CHO)C$_6$H$_4$ (**d**); SiMe$_3$ (**e**); H (**f**)

Reagents and conditions: *i.* I$_2$, HIO$_3$, 30% H$_2$SO$_4$, 80% AcOH, 65 °C; *ii.* (for **3a—c, e**) PhPdI(PPh$_3$)$_2$, CuI, NEt$_3$, 70—75 °C; *iii.* (for **3d**) Pd(OAc)$_2$—2.5 PPh$_3$, CuI, NEt$_3$, 70—75 °C; *iv.* K$_2$CO$_3$, EtOH, 20 °C; *v.* KOH, EtOH, 80 °C.

with cyclization of amides of acetylenylpyrazolecarboxylic acids[14] because test experiments demonstrated that the yields and purities of the cyclization products formed under these conditions were higher than those obtained using Castro's method[7] (CuC≡CPh or CuI in DMF). In addition, cyclization in the presence of KOH was accompanied by the removal of the protective acetyl group, which is in agreement with the published data.[8] Indolocrown ethers **5a—c,f** were obtained in 30—75% yields. Compound **4d** underwent resinification under various conditions of cyclization (CuC≡CPh in DMF or KOH in EtOH).

To summarize, *o*-alkynyl derivatives of *N*-acetylaminobenzo-12-crowns-4 undergo cyclization under the action of KOH in EtOH to form the corresponding 5,6-indole-12-crowns-4 with the simultaneous removal of the acetyl group.

Experimental

The ^{1}H NMR spectra were recorded on a Bruker Avance-300 spectrometer (the assignment of the signals for the protons in the aromatic rings was made based on their chemical shifts calculated according to the additive scheme). The IR spectra were measured on a Bruker IFS-66 spectrometer in KBr pellets. The mass spectra were obtained on a Finnigan SSQ-710 instrument using a direct inlet system (EI, the temperature of the ionization chamber was 220—270 °C, the ionizing voltage was 70 eV). Column chromatography was carried out on KSK silica gel (60/200 μm). The course of the reactions and the purities of the compounds were monitored by TLC on Silufol UV-254 plates. 4-Ethynylbenzaldehyde,[22] 4-nitrophenylacetylene,[23] the PhPdI(PPh$_3$)$_2$ complex,[24] 4-methoxyphenylacetylene,[25,26] and 4´-aminobenzo-12-crown-4 [27] were prepared according to known procedures. Phenylacetylene (Aldrich), trimethylsilylacetylene (Fluka), CuI, PPh$_3$, and Pd(OAc)$_2$ (all purchased from Lancaster) were used without additional purification. Other reagents and organic solvents were prepared according to standard procedures.[28]

***N*-(2,3,5,6,8,9-Hexahydro-1,4,7,10-tetraoxabenzocyclododecen-12-yl)acetamide (1).** Ac$_2$O (4.0 mL, 43 mmol) was added to a solution of 4´-aminobenzo-12-crown-4 (4.1 g, 17 mmol) in dry benzene (30 mL) at ~20 °C. The precipitate that formed was filtered off and recrystallized from a benzene—hexane mixture. Compound **1** was obtained in a yield of 4.75 g (99%), m.p. 102.5—104.5 °C. ^{1}H NMR (CD$_2$Cl$_2$), δ: 2.12 (s, 3 H, Me); 3.71—3.79 (m, 8 H, 4 OCH$_2$); 4.05—4.15 (m, 4 H, 2 ArOCH$_2$); 6.90—6.98 (m, 2 H, H(13), H(14)); 7.14 (br.s, 1 H, NH); 7.31 (s, 1 H, H(11)). IR, ν/cm^{-1}: 1655 (C=O); 3330 (NH). Found (%): C, 59.57; H, 6.80; N, 4.99. C$_{14}$H$_{19}$NO$_5$. Calculated (%): C, 59.78; H, 6.81; N, 4.98.

***N*-(13-Iodo-2,3,5,6,8,9-hexahydro-1,4,7,10-tetraoxabenzocyclododecen-12-yl)acetamide (2).** A mixture of I$_2$ (0.56 g, 2 mmol) and HIO$_3$ (0.19 g, 1 mmol) was added to a solution of compound **1** (1.4 g, 5 mmol) in 80% AcOH (15 mL) and 30% H$_2$SO$_4$ (5 mL). The reaction mixture was stirred at 65 °C for 10 h, diluted with water (30 mL), and extracted with CHCl$_3$. The extract was washed with water and a 10% solution of NaHSO$_3$ and dried with Na$_2$SO$_4$. The solvent was removed *in vacuo* and the residue was recrystallized from a benzene—hexane mixture. Compound **2** was obtained in a yield of 1.3 g (65%), m.p. 145—147 °C. ^{1}H NMR (CD$_2$Cl$_2$), δ: 2.19 (s, 3 H, Me); 3.59—3.87 (m, 8 H, 4 OCH$_2$); 4.09—4.18 (m, 4 H, 2 ArOCH$_2$); 7.25 (br.s, 1 H, NH); 7.39 (s, 1 H, H(11)); 7.87 (s, 1 H, H(14)). IR, ν/cm^{-1}: 1650 (C=O); 3238 (NH). Found (%): C, 41.25; H, 4.29; N, 3.43. C$_{14}$H$_{18}$INO$_5$. Calculated (%): C, 41.29; H, 4.46; N, 3.44.

***N*-[13-(2-Phenylethynyl)-2,3,5,6,8,9-hexahydro-1,4,7,10-tetraoxabenzocyclododecen-12-yl]acetamide (4a).** A mixture of iodide **2** (1.0 g, 2.5 mmol), phenylacetylene (**3a**) (0.33 g, 3.3 mmol), PhPdI(PPh$_3$)$_2$ (40 mg, 0.044 mmol), and CuI (15 mg, 0.15 mmol) in Et$_3$N (2 mL) and benzene (10 mL) was stirred under Ar at 70—75 °C for 20 min. The cooled reaction mixture was filtered through a layer of SiO$_2$ (2.5×2 cm), the solvent was removed *in vacuo*, and the residue was recrystallized from a benzene—hexane mixture. Compound **3a** was obtained in a yield of 0.6 g (65%), m.p. 145—146 °C. ^{1}H NMR (CDCl$_3$), δ: 2.27 (s, 3 H, Me); 3.82—3.95 (m, 8 H, 4 OCH$_2$); 4.18—4.31 (m, 4 H, 2 $ArOCH_2$); 7.18 (s, 1 H, H(14)); 7.39—7.47 (m, 3 H, H(3´), H(4´), H(5´)); 7.51—7.59 (m, 2 H, H(2´), H(6´)); 7.92 (br.s, 1 H, NH); 8.19 (s, 1 H, H(11)). IR, ν/cm^{-1}: 1659 (C=O); 2213 (C≡C); 3285 (NH). Found (%): C, 69.27; H, 6.06; N, 3.74. $C_{22}H_{23}NO_5$. Calculated (%): C, 69.27; H, 6.08; N, 3.67.

Compounds **4b,c,e** were prepared analogously to compound **4a**.

***N*-{13-[2-(4-Methoxyphenyl)ethynyl]-2,3,5,6,8,9-hexahydro-1,4,7,10-tetraoxabenzocyclododecen-12-yl}acetamide (4b).** The yield was 82%, m.p. 85—87 °C (benzene—hexane). ^{1}H NMR ($CDCl_3$), δ: 2.26 (s, 3 H, Me); 3.80—3.95 (m, 11 H, 4 OCH_2, OMe); 4.18—4.29 (m, 4 H, 2 $ArOCH_2$); 6.95 (d, 2 H, H(3´), H(5´), *J* = 8.3 Hz); 7.15 (s, 1 H, H(4)); 7.49 (d, 2 H, H(2´), H(6´), *J* = 8.3 Hz); 7.91 (br.s, 1 H, NH); 8.18 (s, 1 H, H(11)). IR, ν/cm^{-1}: 1660 (C=O); 2218 (C≡C); 3287 (NH). Found (%): C, 66.71; H, 5.80; N, 3.47. $C_{23}H_{25}NO_6$. Calculated (%): C, 67.14; H, 6.12; N, 3.40.

***N*-{13-[2-(4-Nitrophenyl)ethynyl]-2,3,5,6,8,9-hexahydro-1,4,7,10-tetraoxabenzocyclododecen-12-yl}acetamide (4c).** The yield was 66%, m.p. 199—200.5 °C (benzene—$CHCl_3$). ^{1}H NMR (CD_2Cl_2), δ: 2.22 (s, 3 H, Me); 3.75—3.89 (m, 8 H, 4 OCH_2); 4.13—4.24 (m, 4 H, 2 $ArOCH_2$); 7.18 (s, 1 H, H(14)); 7.69 (d, 2 H, H(2´), H(6´), *J* = 8.6 Hz); 7.69 (br.s, 1 H, NH); 8.09 (s, 1 H, H(11)); 8.25 (d, 2 H, H(3´), H(5´), *J* = 8.6 Hz). IR, ν/cm^{-1}: 1664 (C=O); 2212 (C≡C); 3278 (NH). Found (%): C, 61.77; H, 5.45; N, 6.21. $C_{22}H_{22}N_2O_7$. Calculated (%): C, 61.96; H, 5.20; N, 6.57.

***N*-{13-[2-(Trimethylsilyl)ethynyl]-2,3,5,6,8,9-hexahydro-1,4,7,10-tetraoxabenzocyclododecen-12-yl}acetamide (4e).** The yield was 41%, m.p. 130—131.5 °C (benzene—hexane). ^{1}H NMR ($CDCl_3$), δ: 0.32 (s, 9 H, $SiMe_3$); 2.23 (s, 3 H, Me); 3.75—3.89 (m, 8 H, 4 OCH_2); 3.77—3.95 (m, 4 H, 2 $ArOCH_2$); 7.08 (s, 1 H, H(14)); 7.92 (br.s, 1 H, NH); 8.15 (s, 1 H, H(11)). IR, ν/cm^{-1}: 1694 (C=O); 2141 (C≡C); 3388 (NH). Found (%): C, 60.89; H, 7.30; N, 3.89. $C_{19}H_{27}NO_5Si$. Calculated (%): C, 60.45; H, 7.21; N, 3.71.

***N*-{13-[2-(4-Formylphenyl)ethynyl]-2,3,5,6,8,9-hexahydro-1,4,7,10-tetraoxabenzocyclododecen-12-yl}acetamide (4d).** A mixture of iodide **2** (0.2 g, 0.5 mmol), 4-ethynylbenzaldehyde (**3d**) (60 mg, 0.5 mmol), $Pd(OAc)_2$ (20 mg, 0.089 mmol), PPh_3 (60 mg, 0.23 mmol), and CuI (10 mg, 0.053 mmol) in Et_3N (0.5 mL) and benzene (5 mL) was stirred under Ar at 70—75 °C for 1 h. After completion of the reaction, the cooled mixture was filtered through a layer of SiO_2 (2.5×2 cm), the solvent was removed *in vacuo*, and the residue was recrystallized from a benzene—hexane mixture. Compound **4d** was obtained in a yield of 0.12 g (60%), m.p. 129—131 °C. ^{1}H NMR ($CDCl_3$), δ: 2.29 (s, 3 H, Me); 3.80—3.95 (m, 8 H, 4 OCH_2); 4.18—4.30 (m, 4 H, 2 $ArOCH_2$); 7.19 (s, 1 H, H (14)); 7.68 (d, 3 H, H(2´), H(6´), *J* = 8.3 Hz); 7.83 (br.s, 1 H, NH); 7.97 (d, 3 H, H(3´), H(5´), *J* = 8.3 Hz); 8.17 (s, 1 H, H(11)); 10.08 (s, 1 H, CHO). IR, ν/cm^{-1}: 1697 (CHO); 1661 (NHC=O); 2205 (C≡C); 3275 (NH). Found (%): C, 67.34; H, 6.66; N, 4.01. $C_{23}H_{23}NO_6$. Calculated (%): C, 67.46; H, 6.66; N, 3.42.

***N*-(13-Ethynyl-2,3,5,6,8,9-hexahydro-1,4,7,10-tetraoxabenzocyclododecen-12-yl)acetamide (4f).** Potassium carbonate (14 mg, 0.1 mmol) was added to a solution of compound **4e** (0.13 g, 0.8 mmol) in 95% EtOH (5 mL). The reaction mixture was stirred at ~20 °C for 3 h, diluted with water (30 mL), and extracted with $CHCl_3$ (3×15 mL). The organic extracts were dried with Na_2SO_4 and filtered through a layer of Al_2O_3 (2.5×2 cm) The solvent was removed *in vacuo* and the residue was recrystallized from benzene. Compound **4f** was obtained in a yield of 0.2 g (83%), m.p. 151—152.5 °C. ^{1}H NMR ($CDCl_3$), δ: 2.24 (s, 3 H, Me); 3.47 (s, 1 H, C≡CH); 3.78—3.97 (m, 8 H, 4 OCH_2); 4.15—4.29 (m, 4 H, 2 $ArOCH_2$); 7.12 (s, 1 H, H(14)); 7.83 (br.s, 1 H, NH); 8.16 (s, 1 H, H(11)). IR, ν/cm^{-1}: 1666 (C=O); 2095 (C≡C); 3263 (≡C—H); 3337 (NH). Found (%): C, 62.89; H, 6.21; N, 4.84. $C_{16}H_{19}NO_5$. Calculated (%): C, 62.94; H, 6.27; N, 4.59.

13-Phenyl-2,3,5,6,8,9-hexahydro-12*H*-[1,4,7,10]tetraoxacyclododeceno[2,3-*f*]indole (5a). KOH (10 mg, 0.17 mmol) was added to a suspension of compound **4a** (0.1 g, 0.26 mmol) in 95% EtOH (5 mL). The reaction mixture was refluxed for 3 h, diluted with water (15 mL), and extracted with $CHCl_3$ (3×10 mL). The organic extracts were dried with Na_2SO_4 and filtered through a layer of Al_2O_3 (2.5×2 cm). The solvent was removed *in vacuo* and the residue was recrystallized from a benzene—hexane mixture. Compound **5a** was obtained in a yield of 70 mg (70%), m.p. 48—49 °C. ^{1}H NMR ($CDCl_3$), δ: 3.78—3.95 (m, 8 H, 4 OCH_2); 4.15—4.29 (m, 4 H, 2 $ArOCH_2$); 6.36 (s, 1 H, H(14)); 7.09 (s, 1 H, H(15)); 7.18 (s, 1 H, H(11)); 7.34—7.41 (m, 3 H, H(3´), H(4´), H(5´)); 7.50—7.56 (m, 2 H, H(2´), H(6´)). IR, ν/cm^{-1}: 3347 (NH). MS, *m/z* (I_{rel} (%)): 339.9 $[M]^+$ (22), 338.8 (100), 251.0 (31), 195.0 (39), 126.0 (9). High-resolution mass spectrum. Found: *m/z* 339.1465 $[M]^+$. $C_{20}H_{21}NO_4$. Calculated: M = 339.14705.

Compounds **5b,c,f** were prepared analogously to compound **5a.**

13-(4-Methoxyphenyl)-2,3,5,6,8,9-hexahydro-12*H*-[1,4,7,10]tetraoxacyclododeceno[2,3-*f*]indole (5b). The yield was 55%, m.p. 218—220 °C (benzene). ^{1}H NMR ($CDCl_3$), δ: 3.73—3.95 (m, 11 H, 4 OCH_2 and OMe); 4.17—4.26 (m, 4 H, 2 $ArOCH_2$); 6.63 (s, 1 H, H(14)); 6.96—7.5 (m, 3 H, H(3´), H(5´), H(15)); 7.23 (s, 1 H, H(11)); 7.57 (d, 2 H, H(2´), H(6´), *J* = 8.4 Hz); 8.12 (br.s, 1 H, NH). IR, ν/cm^{-1}: 3424 (NH). MS, *m/z* (I_{rel} (%)): 369.0 $[M]^+$ (100), 281.1 (38), 225.1 (41), 140.5 (15). High-resolution mass spectrum. Found: *m/z* 369.1580 $[M]^+$. $C_{21}H_{23}NO_5$. Calculated: M = 369.15761.

13-(4-Nitrophenyl)-2,3,5,6,8,9-hexahydro-12*H*-[1,4,7,10]tetraoxacyclododeceno[2,3-*f*]indole (5c). The yield was 70%, m.p. 251—253 °C (AcOEt). ^{1}H NMR (DMSO-d_6), δ: 3.68—3.95 (m, 8 H, 4 OCH_2); 4.15—4.28 (m, 4 H, 2 $ArOCH_2$); 7.07 (s, 1 H, H(14)); 7.55 (d, 2 H, H(2´), H(6´), *J* = 8.5 Hz); 7.61 (s, 1 H, H(15)); 8.02 (s, 1 H, H(11)); 8.25 (d, 2 H, H(3´), H(5´), *J* = 8.5 Hz). IR, ν/cm^{-1}: 3385 (NH). MS, *m/z* (I_{rel} (%)): 384.0 $[M]^+$ (65), 378.8 (100), 236.0 (31), 175.0 (39), 116.0 (9). High-resolution mass spectrum. Found: *m/z* 384.1320 $[M]^+$. $C_{20}H_{20}N_2O_6$. Calculated: M = 384.13412.

2,3,5,6,8,9-Hexahydro-12*H*-[1,4,7,10]tetraoxacyclododeceno[2,3-*f*]indole (5f). Compound **5f** was prepared from **4e** in 75% yield and from **4f** in 33% yield, m.p. 180—182 °C (benzene—hexane). ^{1}H NMR ($CDCl_3$), δ: 3.75—4.00 (m, 8 H, 4 OCH_2); 4.15—4.22 (m, 4 H, 2 $ArOCH_2$); 6.47 (d, 1 H, H(14), *J* = 2.5 Hz); 7.04 (s, 1 H, H(15)); 7.16 (d, 1 H, H(13), *J* = 2.5 Hz); 7.27 (s, 1 H, H(11)); 8.05 (br.s, 1 H, NH). IR, ν/cm^{-1}: 3347 (NH). MS, *m/z* (I_{rel} (%)): 263.0 $[M]^+$ (100), 175.1 (81), 119.0 (77), 91.0 (21). High-resolution mas spectrum. Found: *m/z* 263.1149 $[M]^+$. $C_{14}H_{17}NO_4$. Calculated: M = 263.11575.

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