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New Multidentate Compounds of Ether-Ester Type

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A series of ether-esters containing multidentate components have been prepared from phenoxyacetic acid. The ligands were synthesized from the appropriate phenoxyacetic acid chloride and various alcohols. Four types of new compounds have been obtained.

(Keywords: Acyclic crown compounds; Ester-ether crown compounds; Multidentate ligands; Phenoxyacetic acid ester)

Neue multidentate Verbindungen vom Ether-Ester-Typ

Eine Reihe von Ether-Estern mit multidentaten Komponenten wurde ausgehend von Phenoxyessigsäure hergestellt. Die Liganden wurden aus den entsprechenden Phenoxyessigsäurechloriden und verschiedenen Alkoholen synthetisiert. Es wurden dabei vier verschiedene neue Typen von multidentaten Verbindungen erhalten.

Introduction

One of our research objectives is to synthesize acyclic multidentate compounds which have potential cation complexing properties similar to those of naturally occuring antibiotics. We have previously reported the preparation of a variety of synthetic phenylenedioxydiacetamide[1,2] ligands which showed a selectivity towards the divalent metal cations.

Results and Discussion

This work reports the synthesis of compounds (**1**-**4**) containing ester and ether moieties in addition to other functional groups. In our previous paper[2] we have reported the preparation of diamide com-

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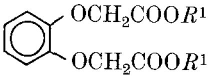
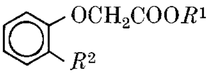
pounds with a structure similar to that of diester **1** from phenylenedioxydiacetyl chloride and amines. The diesters **1 a** and **1 b** were prepared by treating the same acid chloride with the alcohol in question. Compounds of type **2** and **3** were synthesized by reaction of *o*-substituted phenols with chloro-acetic acid to give phenoxyacetic acid and this acid was than transferred to its acid chloride by the treatment with thionyl chloride. The acid chloride thus formed could condense with the appropriate alcohol or glycol to give the ligands **2** and **3**.



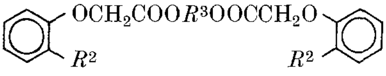
1

a $R^1 = —Bu$
b $R^1 = —CH_2CH_2OCH_2CH_2OBu$



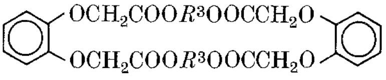
2

c $R^2 = —H$
d $R^2 = —OMe$
e $R^2 = —NO_2$

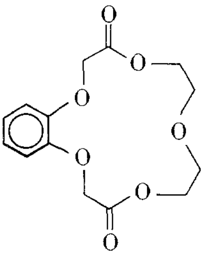


3

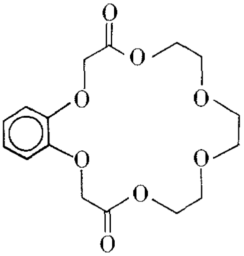
$R^3 = —CH_2CH_2OCH_2CH_2—$



4



5



6

Reaction of the phenylenedioxydiacetyl chloride with the appropriate glycol under high dilution condition gave the monomeric lactones **5** and **6** as the only isolated product. In an effort to prepare the cyclic dimeric lactone of type **4** the same reaction was carried out in much more concentrated solution; however, the monomeric product was still the only isolated product besides the polymeric material. Mass spectra showed molecular ion peaks at m/e; 296 for **5** and 340 for **6** and high resolution mass spectra confirm the molecular formulas for **5** and **6**.

The structure proposed for compounds **1**–**4** are consistent with those determined from the NMR and IR spectra and elemental analysis. The ester carbonyls all exhibited IR bands at 1750–1770 cm^{-1}. All compounds exhibited NMR peaks at δ 4.7 for the —OCH_2CO— group, 4.3 for the —$COOCH_2$— group, 3.7 for —CH_2O— and ca. 6.85 for the aromatic protons.

Acknowledgement

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Experimental

Ultraviolet spectra were taken in methanol on a Perkin Elmer model 356 spectrophotometer. The nuclear magnétic resonance spectra were measured in $CDCl_3$ solution with a Hitachi Perkin Elmer R 20 B spectrometer and *TMS* was used as internal reference. Mass spectra were taken on a Varian MAT-CH 5 mass spectrometer. The infrared spectra were taken on a Perkin Elmer model 180 spectrophotometer.

All solvents used were dried by distillation and if necessary they were purified by following the procedure mentioned in Ref.[3]. All inorganic salts were reagent grade.

Starting Materials

Phenylenedioxydiacetyl chloride was prepared as reported[2]. *o*-Substituted phenoxyacetic acid was synthesized by following the procedure mentioned in Ref.[3]. *o*-Substituted phenoxyacetyl chloride was prepared in the same way as in the synthesis of phenylenedioxydiacyl chloride[2].

Dibutyl 1,2-Phenylenedioxydiacetate (**1 a**)

1,2-Phenylenedioxydiacetyl chloride (1.32 g, 0.0050 mol) was dissolved in 15 ml of carbon tetrachloride and a solution of *n*-butanol (1.5 ml, 0.020 mol) in 10 ml of carbon tetrachloride was added slowly at room temperature. The resulting reaction mixture was kept stirring at the same temperature overnight. After the reaction, the mixture was washed with 10% sodium hydroxide solution several times and than washed with water. The solution was dried over anhydrous sodium sulfate and the solvent was removed to give a light yellow oil, 1.32 g (79% yield); IR: 1750, 1580, 1160 (broad) cm^{-1}; NMR: δ 0.8–1.73 (m, 14 H), 4.16 (t, 4 H, $J = 6.0$ Hz), 4.65 (s, 4 H), 6.88 (s, 4 H); UV: λ_{max} 271 nm, $\varepsilon = 1886$. Cald. for $C_{18}H_{26}O_6$: C 63.90, H 7.69. Found: C 63.75, H 7.40.

Dibutoxyethoxyethyl 1,2-phenylenedioxydiacetate (**1 b**)

The above procedure was followed using butoxyethoxyethanol and the same acid chloride to give a light yellow oil, 1.95 g (76% yield); IR: 1 750, 1 580, 1 100; NMR: δ 0.9-1.68 (m, 14 H), 3.35-3.78 (m, 16 H), 4.26-4.42 (m, 4 H), 4.72 (s, 4 H), 6.9 (s, 4 H); UV: λ_{max} 271 nm, ε = 1 276. Cald. for $C_{26}H_{38}O_{10}$: C 61.18 H 7.45. Found: C 61.32 H 7.20.

Butoxylethoxyethyl phenoxyacetate (**2 bc**)

Phenoxyacetyl chloride (3.07 g, 0.018 mol) was dissolved in 20 ml of dry chloroform and a solution of butoxyethoxyethanol (2.75 g, 0.018 mol) in 20 ml of dry chloroform was added, the mixture was refluxed for 12 h. The resulting mixture was worked up in the same procedure as mentioned above. A colorless oil (3.0 g, 59.61% yield) was isolated; IR: 1 755, 1 600, 1 200 (broad); NMR: δ 0.80-1.70 (m, 7 H), 3.33-3.78 (m, 8 H), 4.28-4.43 (m, 2 H), 4.63 (s, 2 H), 6.80-7.40 (m, 5 H); UV: λ_{max} 270 nm, ε = 1 481; 275 nm, ε = 1 226. Cald. for $C_{16}H_{24}O_5$: C 64.84 H 8.16. Found: C 65.07 H 8.18.

Butoxyethoxyethyl o-methoxyphenoxacetate (**2 bd**)

The above procedure was followed using *o*-methoxyphenoxyacetyl chloride (4 g, 0.02 mol) and butoxyethoxyethanol (3.24 g, 0.02 mol) to give a colorless oil (4.5 g, 69.01% yield); IR: 1 760, 1 590, 1 130, 1 250; NMR: δ 0.78-1.65 (m, 7 H), 3.3-3.9 (m, 8 H), 3.8 (s, 3 H), 4.2-4.45 (m, 2 H), 4.65 (s, 2 H), 6.82 (s, 4 H); UV: λ_{max} 272 nm, ε = 2 588. Cald. for $C_{17}H_{26}O_6$: C 62.56, H 8.03. Found: C 62.36 H 8.06.

Butoxyethoxyethyl o-nitrophenoxyacetate (**2 be**)

The above procedure was followed using *o*-nitrophenoxyacetyl chloride (3.18 g, 0.0148 mol) and butoxyethoxyethanol (3.39 g, 0.0148 mol) to give a colorless oil (3.38 g, 66.89% yield); IR: 1 760, 1 610, 1 525, 1 350, 1 100 (broad); NMR: δ 0.78-1.65 (m, 7 H), 3.34-3.78 (m, 8 H), 4.27-4.42 (m, 2 H), 4.79 (s, 2 H), 6.9-7.9 (m, 4 H); UV: λ_{max} 315 nm, ε = 2 070; 250 nm, ε = 3 344. Cald. for $C_{16}H_{23}NO_3$: C 56.30 H 6.79 N 4.10. Found: C 56.21 H 6.76 N 4.09.

1,11-Diphenoxy-3,6,9-trioxaundecane-2,10-dione (**3 c**)

The above procedure was followed using phenoxyacetyl chloride (3 g, 0.017 mol) and diethylene glycol (0.9 g, 0.0085 mol) to give a colorless oil (2.22 g, 69.83% yield); IR: 1 750, 1 595, 1 200, (broad), 1 180; NMR: δ 3.54-3.70 (m, 4 H); 4.22-4.38 (m, 4 H), 4.62 (s, 4 H), 6.78-7.38 (m, 10 H); UV: λ_{max} 288 nm, ε = 2 906; 295 nm, ε = 2 428. Cald. for $C_{20}H_{22}O_7$: C 64.16 H 5.92. Found: C 63.90 H 5.84.

1,11-Di(o-methoxyphenoxy)-3,6,9-trioxaundecane-2,10-dione (**3 d**)

The above procedure was followed using *o*-methoxyphenoxyacetyl chloride (2.98 g, 0.015 mol) and diethylene glycol (0.79 g, 0.0075 mol) to give white crystals upon recrystalliation from methanol (2.35 g, 72.75% yield), m.p. 58-60 °C; IR: 1 760; 1 590, 1 200 (broad), 1 160; NMR: δ 3.53-3.70 (m, 4 H), 3.84 (s, 6 H), 4.21-4.37 (m, 4 H), 4.69 (s, 4 H), 6.85 (s, 8 H); UV: λ_{max} 272 nm, ε = 3 928. Cald. for $C_{22}H_{26}O_9$: C 60.82 H 6.03. Found: C 60.57 H 5.89.

1,11-Di(o-nitrophenoxy)-3,6,9-trioxandecane-2,10-dione (**3e**)

The above procedure was followed using *o*-nitrophenoxyacetyl chloride (6.88 g, 0.032 mol) and diethyleneglycol (1.70 g, 0.016 mol) to give light brown crystal; recrystallization from methanol gave light yellow crystals (5.84 g, 83.38 yield), m.p. 56-58 °C; IR: 1760, 1600, 1525, 1355, 1200, 1060; NMR: δ 3.58-3.72 (m, 4 H), 4.23-4.39 (m, 4 H), 4.80 (s, 4 H); 6.88-7.85 (m, 8 H); UV: λ_{max} 310 nm, $\varepsilon = 3901$; 252 nm, $\varepsilon = 6369$. Cald. $C_{20}H_{20}N_2O_4$: C 51.73 H 4.14 N 6.03. Found: C 51.57 H 4.34 N 6.14.

2,3-Benzo-1,4,7,10,13-pentaoxa-2-cyclopentadecene-6,14-dione (**5**)

Following the same procedure, phenylenedioxydiacetyl chloride (3.45 g, 0.013 mol) and diethyleneglycol (0.013 mol) were used. The crude product (2.89 g, 75% yield) was a light yellow oil; IR: 1730, 1600, 1230 (broad), 1180; NMR: δ 3.50-3.68 (m, 4 H), 4.15-4.35 (m, 4 H), 4.68 (s, 4 H); UV: λ_{max} 270 nm, $\varepsilon = 1539$; MS: *m*/e 296 (M^+) for $C_{14}H_{16}O_7$.

2,3-Benzo-1,4,7,10,13,16-mexaoxa-2-cycloactadecene-6,17-dione (**6**)

Following the same procedure, phenylenedioxydiacetyl chloride (3.45 g, 0.013 mol) and triethylene glycol (0.013 mol) were used. The crude product (3.54 g, 80% yield) was a yellow oil; IR: 1725, 1580, 1100 (broad); NMR: δ 3.58 (broad singlet, 8 H), 4.25 (broad singlet, 4 H), 4.69 (s, 4 H), 6.86 (4 H); UV: λ_{max} 272 nm, $\varepsilon = 1645$; MS: *m*/e 340 (M^+) for $C_{16}H_{20}O_8$.

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