Synthesis of Lariat Ethers with Pendent *N,N*-Dialkyl Oxyacetamide Groups

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Synthetic routes to thirty crown ether compounds with pendent *N,N*-dialkylamide groups are reported. The new lariat ethers are based on *sym*-(R)dibenzo-13-crown-4-oxyacetamide, *sym*-(R)dibenzo-14-crown-4-oxyacetamide and *sym*-(R)dibenzo-16-crown-5-oxyacetamide, in which R = H or alkyl, and *sym*-(propyl)dicyclohexano-16-crown-5-oxacetamide. Two acyclic polyether analogues with pendent *N,N*-dialkylamide groups are also prepared.

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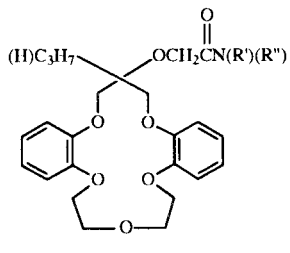
Introduction.

A wide variety of macrocyclic polyether compounds (crown ethers) have been prepared and employed in alkali and alkaline earth metal cation determination and separation due to their superior binding ability for these metal ions [1-3]. Attachment of one or more side arms with potential metal ion coordination sites produces complexing agents which are known as lariat ethers [4]. The coordinating properties of amide groups are well known [5]. We and other researchers have prepared crown ether, monoaza crown ether and diazacrown ether compounds with pendent amide, *N*-alkylamide and *N,N*-dialkylamide functionalities [6-11].

We have reported previously the synthesis of a series of crown ether compounds with pendent amide groups **1** consisting of *sym*-dibenzo-16-crown-5-oxyacetamide and *sym*-(propyl)dibenzo-16-crown-5-oxyacetamide and their *N*-alkyl and *N,N*-dialkyl derivatives [11]. Subsequently the responses of these ionophores toward alkali and alkaline earth metal cations, protons and ammonium ions in solvent polymeric membrane electrodes were assessed [12-14]. It was found that lariat ethers with a *N,N*-dipentyloxyacetamide group as the side arm and a geminal propyl group exhibited high sodium/potassium selectivities with good selectivities for sodium over the other alkali metal cations, alkaline earth cations, protons and ammonium ions.

For further investigation of the influence of structural variation for lariat ether amide ionophores in solvent polymeric membrane electrodes, thirty new crown ether compounds with pendent *N,N*-dialkyloxyacetamide groups have been synthesized. In addition to variation of the geminal group on the central carbon of the three-carbon bridge to include both linear and branched alkyl groups, the crown ether unit has been varied to include dibenzo-13-crown-4, dibenzo-14-crown-4 and dicyclohexano-16-crown-5 rings, as well as the dibenzo-16-crown-5 system. To serve as model compounds, two acyclic polyethers with *N,N*-dipentyloxyacetamide groups and *N,N*-dipentyl 2-(naphthoxy)acetamide have also been prepared. The synthesis of these thirty three new compounds is now described.



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Results and Discussion.

Together with the previously reported *N,N*-dipentyl-*sym*-dibenzo-16-crown-5-oxyacetamide and *N,N*-pentyl-*sym*-(propyl)dibenzo-16-crown-5-oxyacetamide [11], the *N,N*-dialkyl lariat ether amides **2-12** form a series of *N,N*-dipentyl-*sym*-(R)dibenzo-16-crown-5-oxyacetamide compounds in which the group geminal to the functional side arm is systematically varied from hydrogen to methyl to ethyl to propyl to butyl to hexyl to octyl to decyl to dodecyl to tetradecyl to hexadecyl to octadecyl to eicosyl. For the synthesis of **2-12**, the corresponding series of carboxylic acids was available from earlier work. The *sym*-(R)dibenzo-16-crown-5-oxyacetic acids were converted into their acid chlorides by reaction with oxalyl chloride in benzene. Reaction of the lariat ether acid chlorides with dipentylamine in benzene gave the desired *N,N*-dipentyl lariat ether amides **2-12** in 82-99% overall yields for the two steps (Table I).

An alternative route (Scheme 1) was utilized for the preparation of the *N,N*-dialkyl-*sym*-(R)dibenzo-16-crown-5-oxyacetamides **13-22**. This group of *N,N*-dialkyl lariat ether amides includes *N,N*-dioctyl-*sym*-(R)dibenzo-16-crown-5-oxyacetamides **13**, **15**, **19** and **21** in which the geminal R group is varied from hydrogen to propyl to isopropyl to neopentyl, respectively, and *N,N*-didecyl-*sym*-

Table I

Yields, Spectral Data and Combustion Analysis Data for Crown Ether Amides **2-31** and Model Amide Compounds **32-34**

Compound	Yield %	mp (°C)	^{1}H NMR Spectrum (200 MHz), ppm [a]	IR Spectrum cm^{-1} [b]	Molecular Formula	Combustion Analysis Theory/Found C	H
2	90	oil	0.80-0.91 (m, 6H), 1.20-1.35 (m, 8H), 1.43-1.60 (m, 7H), 3.23-3.36 (m, 4H), 3.95 (s, 4H), 4.10-4.34 (m, 8H), 4.58 (s, 2H), 6.81-7.00 (m, 8H)	1644 (C=O), 1257, 1123 (C-O)	$C_{32}H_{47}NO_7$	68.91 69.18	8.49 8.35
3	98	oil	0.78-0.91 (m, 6H), 1.00-1.08 (t, 3H), 1.28 (m, 8H), 1.40-1.60 (m, 4H), 1.96-2.10 (m, 2H), 3.23-3.35 (m, 4H), 3.90-3.94 (m, 4H), 4.13-4.21 (m, 6H), 4.36-4.41 (d, 2H), 4.59 (s, 2H), 6.81-6.94 (m, 8H)	1632 (C=O), 1255, 1114 (C-O)	$C_{33}H_{49}NO_7$	69.33 69.28	8.64 8.41
4	97	oil	0.78-0.98 (m, 9H), 1.23-1.51 (m, 16H), 1.96-2.04 (t, 2H), 3.23-3.35 (m, 4H), 3.90-3.94 (m, 4H), 4.07-4.21 (m, 6H), 4.36-4.41 (d, 2H), 4.59 (s, 2H), 6.80-6.98 (m, 8H)	1644 (C=O), 1257, 1122 (C-O)	$C_{35}H_{53}NO_7$	70.09 70.46	8.91 8.86
5	99	oil	0.78-0.90 (m, 9H), 1.25-1.48 (m, 20H), 1.95-1.99 (d, 2H), 3.22-3.35 (m, 4H), 3.92 (s, 4H), 4.15-4.20 (d, 6H), 4.35-4.41 (d, 2H), 4.59 (s, 2H), 6.81-6.94 (m, 8H)	1644 (C=O), 1257, 1122 (C-O)	$C_{37}H_{57}NO_7$	70.83 71.15	9.16 9.10
6	89	oil	0.78-0.91 (m, 9H), 1.15-1.60 (m, 24H), 1.95-2.05 (t, 2H), 3.20-3.40 (m, 4H), 3.91-3.95 (m, 4H), 4.15-4.20 (m, 6H), 4.36-4.41 (d, 2H), 4.59 (s, 2H), 6.81-6.94 (m, 8H)	1644 (C=O), 1257, 1122 (C-O)	$C_{39}H_{61}NO_7$	71.42 71.74	9.37 8.99
7	94	oil	0.78-0.91 (m, 9H), 1.26-1.48 (m, 28H), 1.94-2.02 (t, 2H), 3.23-3.35 (m, 4H), 3.90-3.94 (m, 4H), 4.15-4.20 (d, 6H), 4.36-4.41 (d, 2H), 4.59 (s, 2H), 6.80-6.98 (m, 8H)	1637 (C=O), 1255, 1114 (C-O)	$C_{41}H_{65}NO_7$	72.00 71.96	9.58 9.37
8	82	oil	0.78-0.90 (m, 9H), 1.26-1.48 (m, 34H), 3.20-3.41 (m, 4H), 3.92-3.94 (d, 4H), 4.15-4.20 (d, 6H), 4.36-4.41 (d, 2H), 4.59 (s, 2H), 6.81-6.96 (m, 8H)	1637 (C=O), 1255, 1120 (C-O)	$C_{43}H_{69}NO_7$	72.54 72.20	9.77 9.46
9	97	oil	0.78-0.90 (m, 9H), 1.10-1.62 (m, 36H), 1.95-1.99 (m, 2H), 3.22-3.35 (m, 4H), 3.92 (s, 4H), 4.15-4.20 (m, 6H), 4.36-4.41 (d, 2H), 4.59 (s, 2H), 6.81-6.96 (m, 8H)	1643 (C=O), 1255, 1114 (C-O)	$C_{45}H_{73}NO_7$	73.03 72.76	9.94 10.00
10	92	oil	0.79-0.90 (m, 9H), 1.05-1.61 (m, 40H), 1.92-2.05 (d, 2H), 3.22-3.34 (m, 4H), 3.92 (s, 4H), 4.15-4.20 (m, 6H), 4.36-4.41 (d, 2H), 4.59 (s, 2H), 6.81-6.95 (m, 8H)	1643 (C=O), 1250, 1114 (C-O)	$C_{47}H_{77}NO_7$	73.49 73.01	10.10 10.22
11	99	oil	0.78-0.91 (m, 9H), 1.10-1.60 (m, 44H), 1.95-1.99 (m, 2H), 3.23-3.35 (m, 4H), 3.92-3.94 (d, 4H), 4.15-4.20 (d, 6H), 4.36-4.41 (d, 2H), 4.59 (s, 2H), 6.80-6.98 (m, 8H)	1643 (C=O), 1255, 1120 (C-O)	$C_{49}H_{81}NO_7$	73.92 73.66	10.25 10.36
12	88	oil	0.79-0.90 (m, 9H), 1.15-1.60 (m, 48H), 1.90-2.15 (s, 2H), 3.22-3.35 (m, 4H), 3.93 (s, 4H), 4.15-4.20 (d, 6H), 4.36-4.41 (d, 2H), 4.59 (s, 2H), 6.81-6.94 (m, 8H)	1643 (C=O), 1255, 1114 (C-O)	$C_{51}H_{85}NO_7$	74.32 73.92	10.39 10.37
13	75	38-39	0.84-0.88 (t, 6H), 1.26-1.35 (m, 20H), 1.73 (s, 4H), 3.19-3.36 (m, 4H), 3.87-4.02 (m, 4H), 4.14-4.18 (m, 4H), 4.26-4.45 (m, 5H), 4.61 (s, 2H), 6.83-7.01 (m, 8H)	1651 (C=O), 1258, 1114 (C-O)	$C_{37}H_{57}NO_7$	70.78 70.87	9.15 9.21

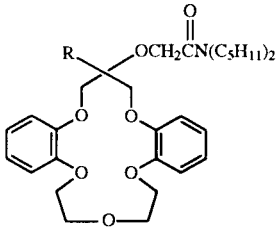
Table 1 (continued)

Compound	Yield %	mp (°C)	^{1}H NMR Spectrum (200 MHz), ppm [a]	IR Spectrum cm^{-1} [b]	Molecular Formula	Combustion Analysis Theory/Found C	H
14	76	56-57	0.84-0.90 (t, 6H), 1.26-1.35 (m, 28H), 1.55 (s, 4H), 3.19-3.36 (m, 4H), 3.92-3.97 (m, 4H), 4.14-4.18 (m, 4H), 4.27-4.39 (m, 5H), 4.61 (s, 2H), 6.82-7.00 (m, 8H)	1651 (C=O), 1258, 1122 (C-O)	$C_{41}H_{65}NO_7$	72.00 72.16	9.58 9.62
15	85	50-51	0.83-1.02 (m, 9H), 1.19-1.25 (m, 20H), 1.49-1.51 (m, 6H), 1.93-2.01 (m, 2H), 3.22-3.35 (m, 4H), 3.90-3.94 (m, 4H), 4.15-4.20 (m, 6H), 4.36-4.40 (d, 2H), 4.59 (s, 2H), 6.80-6.93 (m, 8H)	1644 (C=O), 1257, 1122 (C-O)	$C_{40}H_{63}NO_7$	71.71 71.90	9.48 9.65
16	70	oil	0.84-1.02 (m, 9H), 1.19-1.25 (m, 28H), 1.49-1.51 (m, 6H), 1.93-2.01 (m, 2H), 3.22-3.29 (m, 4H), 3.90-3.94 (m, 4H), 4.15-4.20 (m, 6H), 4.35-4.40 (d, 2H), 4.59 (s, 2H), 6.80-6.93 (m, 8H)	1645 (C=O), 1240, 1130 (C-O)	$C_{44}H_{71}NO_7$	72.78 72.56	9.86 9.80
17	76	100-101	0.76-0.90 (m, 6H), 1.10-1.26 (m, 14H), 1.40-1.51 (m, 4H), 2.60 (m, 1H), 3.24-3.36 (m, 4H), 3.88-3.92 (m, 4H), 4.13-4.27 (m, 6H), 4.48-4.53 (d, 2H), 4.66 (s, 2H), 6.78-8.97 (m, 8H)	1644 (C=O), 1256, 1122 (C-O)	$C_{34}H_{51}NO_7$	69.71 69.33	8.78 8.65
18	76	119-120	0.78-0.89 (m, 6H), 1.13-1.25 (m, 18H), 1.43-1.47 (m, 4H), 2.60 (m, 1H), 3.20-3.36 (m, 4H), 3.88-3.92 (m, 4H), 4.13-4.27 (m, 6H), 4.48-4.53 (d, 2H), 4.67 (s, 2H), 6.78-6.97 (m, 8H)	1642 (C=O), 1257, 1122 (C-O)	$C_{36}H_{55}NO_7$	70.44 70.80	9.03 9.18
19	77	59-60	0.83-0.89 (m, 6H), 1.14-1.24 (m, 26H), 1.47-1.55 (m, 4H), 2.57-2.64 (m, 1H), 3.21-3.36 (m, 4H), 3.89-3.91 (m, 4H), 4.14-4.27 (m, 6H), 4.49-4.54 (d, 2H), 4.67 (s, 2H), 6.80-6.97 (m, 8H)	1644 (C=O), 1256, 1122 (C-O)	$C_{40}H_{63}NO_7$	71.70 71.97	9.48 9.91
20	72	51-52	0.84-0.90 (m, 6H), 1.13-1.24 (m, 34H), 1.46-1.55 (m, 4H), 2.56-2.63 (m, 1H), 3.20-3.35 (m, 4H), 3.89-3.91 (m, 4H), 4.13-4.26 (m, 6H), 4.48-4.53 (d, 2H), 4.66 (s, 2H), 6.78-6.97 (m, 8H)	1645 (C=O), 1257, 1122 (C-O)	$C_{44}H_{71}NO_7$	72.78 72.96	9.86 9.95
21	73	oil	0.75-1.65 (m, 41H), 3.18-3.41 (m, 4H), 3.80-4.30 (m, 10H), 4.41-4.52 (d, 2H), 4.60 (s, 2H), 6.73-7.00 (m, 8H),	1643 (C=O), 1253, 1118 (C-O)	$C_{42}H_{67}NO_7$	72.26 71.86	9.68 9.90
22	76	oil	0.70-1.65 (m, 49H), 3.10-3.44 (m, 4H), 3.72-4.28 (m, 10H), 4.40-4.51 (d, 2H), 4.62 (s, 2H), 6.71-7.00 (m, 8H),	1643 (C=O), 1251, 1117 (C-O)	$C_{46}H_{75}NO_7$	73.25 73.65	10.03 10.43
23	90	oil	0.80-2.25 (m, 53H), 3.08-4.25 (m, 20H), 4.25-4.48 (m, 2H)	1647 (C=O), 1111 (C-O)	$C_{40}H_{75}NO_7$	70.44 70.19	11.08 11.29
24	93	oil	0.75-2.00 (m, 60H), 3.10-3.85 (m, 20H), 4.25-4.42 (m, 2H)	1648 (C=O), 1111 (C-O)	$C_{44}H_{83}NO_7 \cdot 0.1CH_2Cl_2$	70.94 70.96	11.23 11.33
25	91	oil	0.83-0.95 (m, 6H), 1.20-1.62 (m, 12H), 3.15-3.32 (m, 4H), 4.00-4.10 (m, 1H), 4.25-4.40 (m, 10H), 6.90-7.10 (m, 8H)	1644 (C=O), 1259, 1113 (C-O)	$C_{29}H_{41}NO_6$	69.71 69.69	8.27 8.42
26	95	oil	0.80-1.00 (m, 9H), 1.10-1.75 (m, 16H), 3.20-3.32 (m, 4H), 4.15-4.41 (m, 10H), 6.95-7.04 (m, 8H)	1643 (C=O), 1256,1114 (C-O)	$C_{32}H_{47}NO_6$	70.95 70.76	8.74 8.96
27	93	oil	0.84-1.00 (t, 6H), 1.20-1.70 (m, 12H), 2.20-2.40 (m, 2H), 3.16-3.35 (m, 4H), 4.10-4.50 (m, 11H), 6.88-7.02 (m, 8H)	1655 (C=O), 1256, 1117 (C-O)	$C_{30}H_{43}NO_6$	70.15 69.75	8.44 8.41
28	82	oil	0.80-1.00 (m, 9H), 1.10-1.70 (m, 14H), 1.75-1.90 (m, 2H), 2.20-2.33 (m, 2H), 3.20-3.38 (m, 4H), 4.10-4.50 (m, 10H), 6.91-7.02 (m, 8H)	1646 (C=O), 1255, 1118 (C-O)	$C_{33}H_{49}NO_6$	71.32 71.64	8.89 8.73
29	75	oil	0.80-1.65 (m, 24H), 2.25-2.40 (m, 3H), 3.20-3.45 (m, 4H), 4.15-4.70 (m, 10H), 6.82-7.03 (m, 8H)	1644 (C=O), 1253, 1118 (C-O)	$C_{33}H_{49}NO_6 \cdot 0.3CH_2Cl_2$	68.81 68.42	8.60 8.25

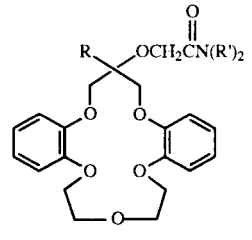
Table 1 (continued)

Compound	Yield %	mp (°C)	^{1}H NMR Spectrum (200 MHz), ppm [a]	IR Spectrum cm^{-1} [b]	Molecular Formula	Combustion Analysis Theory/Found C	H
30	88	oil	0.82-1.00 (m, 9H), 1.10-1.65 (m, 28H), 1.80-1.95 (m, 2H), 2.22-2.35 (m, 2H), 3.21-3.40 (m, 4H), 4.25-4.50 (m, 10H), 6.85-7.05 (m, 8H)	1647 (C=O), 1255, 1118 (C-O)	$C_{40}H_{63}NO_6$	73.47 73.33	9.71 9.79
31	93	oil	0.77-0.98 (m, 6H), 1.10-1.62 (m, 12H), 2.25-2.45 (m, 2H), 3.15-3.30 (m, 4H), 4.15-4.40 (m, 6H), 4.52-4.57 (d, 2H), 4.69-4.74 (d, 2H), 6.82-6.94 (m, 8H), 7.30-7.50 (m, 3H), 7.73-7.78 (m, 2H)	1644 (C=O), 1253, 1118 (C-O)	$C_{36}H_{47}NO_6$	73.32 73.47	8.03 7.78
32	89	oil	0.82-1.00 (m, 6H), 1.15-1.65 (m, 12H), 3.17-3.28 (m, 4H), 3.82 (s, 6H), 4.25-4.50 (m, 5H), 4.55 (s, 2H), 6.86-7.00 (m, 8H)	1654 (C=O), 1254, 1126 (C-O)	$C_{29}H_{43}NO_6$	69.43 69.20	8.64 8.42
33	93	oil	0.80-1.95 (m, 25H), 3.20-3.32 (m, 4H), 3.75 (s, 6H), 4.11-4.25 (m, 4H), 4.39 (s, 2H), 6.82-7.00 (m, 8H)	1646 (C=O), 1254, 1126 (C-O)	$C_{32}H_{49}NO_6$• $0.2H_2O$	70.22 70.01	9.10 8.79
34	100	oil	0.81-0.85 (m, 6H), 1.22-1.34 (m, 12H), 1.51-1.65 (m, 4H), 4.79 (s, 2H), 7.16-7.78 (m, 7H)	1650 (C=O), 1255, 1217 (C-O)	$C_{22}H_{31}NO_2$	77.38 77.29	9.15 9.20

[a] In deuteriochloroform. [b] Deposited from deuteriochloroform solution onto a sodium chloride plate.



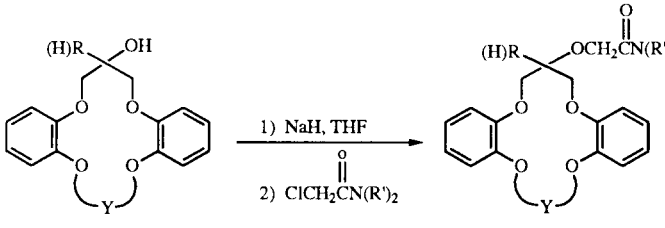
	R
2	CH_3
3	C_2H_5
4	C_4H_9
5	C_6H_{13}
6	C_8H_{17}
7	$C_{10}H_{21}$
8	$C_{12}H_{25}$
9	$C_{14}H_{29}$
10	$C_{16}H_{33}$
11	$C_{18}H_{37}$
12	$C_{20}H_{41}$



	R	R'
13	H	C_8H_{17}
14	H	$C_{10}H_{21}$
15	C_3H_7	C_8H_{17}
16	C_3H_7	$C_{10}H_{21}$
17	$CH(CH_3)_2$	C_5H_{11}
18	$CH(CH_3)_2$	C_6H_{13}
19	$CH(CH_3)_2$	C_8H_{17}
20	$CH(CH_3)_2$	$C_{10}H_{21}$
21	$CH_2C(CH_3)_3$	C_8H_{17}
22	$CH_2C(CH_3)_3$	$C_{10}H_{21}$

(R)dibenzo-16-crown-5-oxyacetamides **14**, **16**, **20** and **22** which provide the same variation of the geminal R group. Contrary to the initial series of lariat ether amides **2-12** in which the structural change in the geminal R group was from hydrogen to linear alkyl groups of increasing length, in these two series the geminal R group variation is from hydrogen to a linear alkyl group to a branched alkyl group.

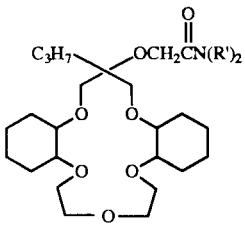
Scheme 1



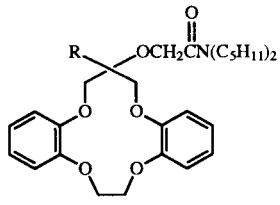
For the preparation of the *N,N*-dialkyl lariat ether amides **13-22**, the requisite *N,N*-dialkyl-2-chloroacetamides were prepared in high yields (>90%) by reaction of the appropriate dialkylamine with chloroacetyl chloride in diethyl ether at -10° [15-18]. Treatment of the *sym*-(hydroxy)(R)dibenzo-16-crown-5 compounds with sodium hydride in tetrahydrofuran then the appropriate *N,N*-dialkyl-2-chloroacetylacetamide (Scheme 1) gave the *N,N*-dialkyl-*sym*-(R)dibenzo-16-crown-5-oxyacetamides **13-22** in 75-85% yields (Table I).

For examination of the structural change from a *N,N*-dialkyl-*sym*-(R)dibenzo-16-crown-5-oxyacetamide to the corresponding *N,N*-dialkyl-*sym*-(R)dicyclohexano-16-crown-5-oxyacetamide, the preparation of *N,N*-dioctyl- and *N,N*-didecyl-*sym*-(propyl)dibenzo-16-crown-5-oxyacetamides (**23** and **24**, respectively) was desired. Two potential routes to such compounds involve: a) coupling of the amide-containing side arm to a dicyclohexano-16-crown-5 precursor, and b) attachment of the amide-containing side arm to a dibenzo-16-crown-5 unit followed by reduction. We have found the latter to be more efficient. Catalytic hydrogenation of *N,N*-dioctyl- and *N,N*-didecyl-*sym*-(propyl)dibenzo-16-crown-5-oxyacetamides **15** and **16** gave high yields of **23** and **24**, respectively (Table I).

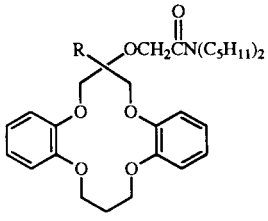
To assess the effect of crown ether ring size upon the behavior of *N,N*-dialkyl lariat ether oxyacetamides in polymeric membrane electrodes, ionophores based upon



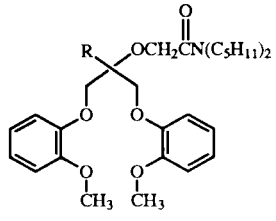
	R
23	C_8H_{17}
24	$C_{10}H_{21}$



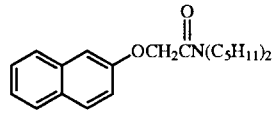
	R
25	H
26	C_3H_7



	R
27	H
28	C_3H_7
29	$CH(CH_3)_2$
30	$C_{10}H_{21}$
31	C_6H_5



	R
32	H
33	C_3H_7



34

dibenzo-13-crown-4 (**25** and **26**) and dibenzo-14-crown-4 (**27-31**) were prepared from the corresponding lariat ether carboxylic acids by reaction with oxalyl chloride in benzene followed by dipentylamine in 75-95% overall yields for the two steps (Table I).

Similarly the *N,N*-dipentyl acyclic polyether amides **32** and **33** and *N,N*-dipentyl(2-naphthoxy)acetamide (**34**) were prepared for use as model compounds from the corresponding carboxylic acids in high yields for the two-step reactions (Table I).

The structures of the new *N,N*-dialkylamide compounds **2-34** were confirmed by ^{1}H nmr and ir spectra and by combustion analysis (Table I). In the ^{1}H nmr spectra of the *N,N*-dialkyl-*sym*-(alkyl)dibenzo-16-crown-5-oxyacetamides **2-12** and **15-22**, *N,N*-dipentyl-*sym*-(propyl)-dibenzo-13-crown-4-oxyacetamide (**26**) and *N,N*-dipentyl-*sym*-(alkyl or phenyl)dibenzo-14-crown-4-oxyacetamides **28-31** clearly discernable AB patterns were evident for the diastereotopic methylene group hydrogens on the three-carbon bridges which demonstrate conformational restrictions of this structural unit on the nmr timescale [11].

EXPERIMENTAL

The ir spectra were obtained with a Perkin Elmer Model 1600 spectrophotometer and are reported in reciprocal centimeters. The ^{1}H nmr spectra were recorded with an IBM AF-200 spectrometer in deuteriochloroform and chemical shifts are reported in parts per million downfield (δ) from TMS. Combustion analysis was performed by Desert Analytics Laboratory (Tucson, Arizona).

Unless specified otherwise, reagent grade reactants and solvents were used as received from commercial suppliers. Tetrahydrofuran was purified by distillation from benzophenone ketyl. Pentane was dried stored over sodium ribbon. *N,N*-Dipentyl-2-chloroacetamide were prepared as described previously [11]. The lariat ether alcohol and carboxylic acid reactants were prepared by the reported methods [19-27].

Preparation of *N,N*-Dihexyl, *N,N*-Dioctyl and *N,N*-Didecyl-2-oxyacetamides.

Literature procedures [15-18] were adapted. A solution of chloroacetyl chloride (0.050 mole) in 250 ml of anhydrous diethyl ether was cooled to -15° in an ice-salt bath. A solution of the dialkylamine (0.10 mole) in 50 ml of anhydrous diethyl ether was added at such a rate that the temperature of the reaction mixture was kept below -10°. The precipitated dialkylamine hydrochloride was removed by filtration and the filtrate was washed successively with 5% hydrochloric acid, 5% sodium bicarbonate and water and dried over magnesium sulfate. The solution was evaporated *in vacuo* with a rotary evaporator and then subjected to oil pump vacuum at 40° for one hour to provide a 95-98% yield of the desired product as an oil.

General Procedure for the Synthesis of *N,N*-Dipentylamides **2-12** and **25-34.**

A mixture of the appropriate carboxylic acid (2.80 mmoles) and 0.50 ml of oxalyl chloride (5.60 mmoles) in 40 ml of anhydrous benzene was stirred at room temperature under nitrogen for 10 hours. The solvent and excess oxalyl chloride were evaporated *in vacuo* to give the crude acid chloride which was used without purification for the next step. To a stirred solution of the crude acid chloride in 40 ml of anhydrous benzene at room temperature under nitrogen, 1.15 ml (5.60 mmoles) of dipentylamine was added slowly with a syringe. After the addition was completed, the mixture was stirred for three hours and then washed with water (2 x 50 ml), 10% hydrochloric acid (2 x 50 ml) and water (2 x 50 ml). The benzene solution was dried over calcium chloride and the solvent was removed *in vacuo* to give the desired product. See Table I for spectral and combustion analysis data for compounds **2-12** and **25-34**,

General Procedure for the Synthesis of *N,N*-Dialkyl-*sym*-(R)-dibenzo-16-crown-5-oxyacetamides **13-22**.

The protecting mineral oil was removed from 1.16 g (0.029 mole) of sodium hydride (60% in mineral oil) by washing with dry pentane under nitrogen. Tetrahydrofuran (250 ml) then the *sym*-(hydroxy)(R)dibenzo-16-crown-5 (0.014 mole) were added and the mixture was stirred magnetically at room temperature for one hour. A solution of the *N,N*-dialkyl-2-chloroacetamide (0.017 mole) in 50 ml of tetrahydrofuran was added dropwise during a two-hour period. After stirring for an additional five hours, the solvent was evaporated *in vacuo* and the residue was dissolved in dichloromethane. The solution was washed with water, dried over magnesium sulfate and evaporated *in vacuo* to give a colorless oil. For compounds **13-15**, **19** and **20**, the oils were crystallized from 80 ml of hexane. For compounds **17** and **18**, the oils were crystallized from 80 ml of hexane-diethyl ether (1:1, v/v). See Table I for spectral and combustion analysis date for **13-22**.

Preparation of *N,N*-Didecyl-*sym*-(propyl)dicyclohexano-16-crown-5-oxyacetamide (**24**).

A mixture of 2.37 g (3.20 mmoles) of **16**, 1.00 g of 5% rhodium on alumina catalyst and 1.00 g of acetic acid in 300 ml of butanol was subjected to 500 psi of hydrogen at 75° for 20 hours. The reaction mixture was filtered through filter paper and evaporated *in vacuo*. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over magnesium sulfate and evaporated *in vacuo*. The residue was dissolved in 100 ml of methanol and filtered through a polytetrafluoroethylene microfilter (0.22 micrometer). Evaporation of the filtrate *in vacuo* gave 2.23 g (93%) of **24** as a colorless oil. See Table I for spectral and combustion analysis data for **24**.

By the same procedure, **15** was hydrogenated to give **23**.

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