Crown Ether Acetals: Synthesis and Characterisation of a Family of Novel Oxygen Macrocyclic Compounds

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The synthesis of cyclic acetals containing a repetitive $-CH_2CH_2O-$ grouping within the ring is described. Compounds with rings of up to thirty-four members and with one or two acetal groups have been prepared and characterised by their ^1H and ^{13}C n.m.r. spectra, the amount of acetaldehyde released on hydrolysis, and their molecular weights. The general formulae of the new compounds are $CH_3CH(OCH_2CH_2)_nO$. with n = 2—6; $CH_3CH(OCH_2CH_2)_nOCH(CH_3)(OCH_2CH_2)_nO$, with n = 2—5; $RCH(OCH_2CH_2)_2O$ with R = Pr, Pr^i, Ph; and $C_6H_4O(CH_2CH_2O)_nCH(CH_3)(OCH_2CH_2)_nO$, with n = 0, 1, 2. As precursors for compounds related to the last of these series, the new open-chain dichloroacetals $CH_3CH[(OCH_2CH_2)_nCl]_2$, with n = 2, 3 were prepared. Rate constants for the acid-catalysed hydrolysis of some of the new acetals are reported.

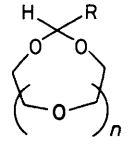
Crown ether acetals [1] are cyclic polyethers that contain one or more groupings of the general form $-O{\cdot}CRR'{\cdot}O-$ as part of the ring (where, most commonly, R = H, R′ = Me). *A priori* they are expected to exhibit cation-binding properties similar to crown ethers containing the same number of oxygen atoms within the multidentate ligand ring.[2,3] However, the two groups of compounds differ in that the ring of crown ether acetals is easily cleaved by acid-catalysed hydrolysis, whereas crown ethers are stable under the same conditions. The open-chain diols produced in the hydrolysis are expected to have a lower capacity for cation-binding.[4] It follows that metal ions are released from metal complexes (' coronates ') on addition of acid, which is expected to prove a useful property of crown ether acetals.

A further point of interest is their potential for reactivity comparisons between metal-complexed and uncomplexed acetals. This aspect is further discussed in another paper.[5]

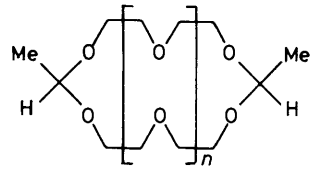
The present report describes the synthesis and characterisation of cyclic ether acetals of the general formula (1) and of some related compounds, as well as that of certain crown compounds, formed as by-products that contain two acetal functions (2).

All the compounds (1) and (2) have the same empirical formula as acetaldehyde, C_2H_4O. Accordingly, combustion analysis is only of very limited help in establishing either the structure or purity of the compounds prepared. Other methods of analysis were more informative, in particular, assays of the amount of acetaldehyde liberated on hydrolysis (the ' acetaldehyde equivalent '), n.m.r. spectra, and molecular-weight determinations, both by vapour pressure osmometry and chemical ionisation mass spectrometry. The systematic study of chemical ionisation mass spectra of members of this group of compounds † revealed a particularly simple pattern for the breakdown of protonated crown ether acetals in the gas phase. These results will be reported and discussed elsewhere.

Some small-ring cyclic acetals have been known since the 19th century,[6,7] and the synthesis of individual examples of cyclic ether acetals or large ring acetals have been reported at various times since then.[8–19] The first large-ring crown ether acetals [not members of either series (1) or (2)] were prepared by Pedersen.[20] They were considered by him in the context of cation binding but were thought to offer no advantages over the stable crown ethers without an acetal grouping.



(1) n = 1-5, R = alkyl or phenyl



(2) n = 1-4

Of the various synthetic methods used, the condensation of aldehyde with diol in the presence of a cation-exchange resin in the acid form, is the simplest procedure. With suitable modifications, this method, first described by Astle *et al.*[10] and later developed by various workers,[15,16,18,19] was found to be applicable to the synthesis of all purely aliphatic crown ether acetals now reported for the first time.

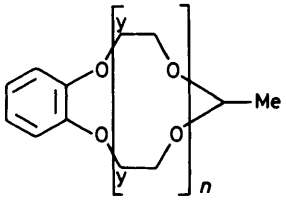
Members of the series of benzo-crown ether acetals (3) were prepared by a modified Williamson ether synthesis from catechol and the complementary dichloroacetal (4). This general approach was first applied to the synthesis of cyclic acetals by Delepine in 1901.[21]

Because of the cumbersome systematic nomenclature of the large rings, we have adapted Pedersen's semi-trivial nomenclature [22] of crown ethers to the present series. For instance, the compound (1; n = 1, R = Me) (2-methyl-1,3,6-trioxacyclo-octane), is accordingly called 2-methyl-8-crown-3 (symbolised as 8-C-3), where the numbers respectively indicate the attachment of the methyl group to the 2-position of an *eight*-membered ring containing *three* oxygen atoms. Other abbreviated names were formed similarly. Table 1 gives the fully systematic and abbreviated names of all new compounds reported in this paper.

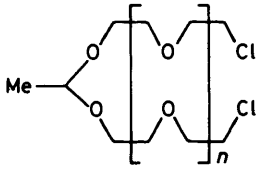
† Measurements were carried out by R. A. Hancock, R. Walder, and H. Weigel, Royal Holloway College.

Table 1. Fully systematic and abbreviated names of new acetals

Compound	Fully systematic name	Abbreviated name	Symbol
(1; n = 2, R = Me)	2-Methyl-1,3,6,9-tetraoxacycloundecane	2-Methyl-11-crown-4	11-C-4
(1; n = 3, R = Me)	2-Methyl-1,3,6,9,12-pentaoxacyclotetradecane	2-Methyl-14-crown-5	14-C-5
(1; n = 4, R = Me)	2-Methyl-1,3,6,9,12,15-hexaoxacycloheptadecane	2-Methyl-17-crown-6	17-C-6
(1; n = 5, R = Me)	2-Methyl-1,3,6,9,12,15,18-heptaoxacycloeicosane	2-Methyl-20-crown-7	20-C-7
(1; n = 1, R = Pr^n)	2-Propyl-1,3,6-trioxacyclo-octane	2-Propyl-8-crown-3	Pr-8-C-3
(1; n = 1, R = Pr^i)	2-Isopropyl-1,3,6-trioxacyclo-octane	2-Isopropyl-8-crown-3	Pr^i-8-C-3
(1; n = 1, R = Ph)	2-Phenyl-1,3,6-trioxacyclo-octane	2-Phenyl-8-crown-3	Ph-8-C-3
(2; n = 1)	2,10-Dimethyl-1,3,6,9,11,14-hexaoxacyclohexadecane	2,10-Dimethyl-16-crown-6	D-16-C-6
(2; n = 2)	2,13-Dimethyl-1,3,6,9,12,14,17,20-octaoxacyclodocosane	2,13-Dimethyl-22-crown-8	D-22-C-8
(2; n = 3)	2,16-Dimethyl-1,3,6,9,12,15,17,20,23,26-decaoxacyclo-octacosane	2,16-Dimethyl-28-crown-10	D-28-C-10
(2; n = 4)	2,19-Dimethyl-1,3,6,9,12,15,18,20,23,26,29,32-dodecaoxa-cyclotetratriacontane	2,19-Dimethyl-34-crown-12	D-34-C-12
(3; n = 0)	2-Methyl-1,3-benzodioxole	Benzo-2-methyl-5-crown-2	B-5-C-2
(3; n = 1)	2,3,7,8-Tetrahydro-5-methyl-1,4,6,9-benzotetraoxaundecin	Benzo-2-methyl-11-crown-4	B-11-C-4
(3; n = 2)	2,3,5,6,10,11,13,14-Octahydro-8-methyl-1,4,7,9,12,15-benzohexaoxacycloheptadecin	Benzo-2-methyl-17-crown-6	B-17-C-6
(4; n = 1)	1,1-Bis[2-(2-chloroethoxy)ethoxy]ethane		CEEE
(4; n = 2)	1,1-Bis{2-[2-(2-chloroethoxy)ethoxy]ethoxy}ethane		CEEEE



(3) n = 0-2



(4) n = 0-2

Table 2. Dependence of yield of monoacetals on concentration of glycol

Concentration of glycol (% w/v)	Yield of 8-C-3 (%)	Yield of 11-C-4 (%)
2.5	29	5
8	15	3
18	8	
20		1

Experimental

The acetals of series (1) and (2) were prepared from acetaldehyde and the corresponding diols. The diol was dissolved in a mixture of light petroleum (b.p. 30—40 °C; 1 dm^3) and dichloromethane (500 cm^3), contained in a large flask fitted with a Dean–Stark separator and condenser, dropping funnel and magnetic stirrer. Amberlite IR-120 (32 g per mole of diol) air-dried sulphonic acid resin was added and the contents were refluxed. Acetaldehyde (1.4 mole per mole of diol) was then slowly added from a dropping funnel and the mixture was refluxed until all the water was removed from the system (24—36 h). For all the preparations the main aim was an optimum yield of compounds (1) [rather than of (2)], which required a low diol concentration, conveniently of *ca.* 2.5—4% (w/v). [The yield of (1) dropped sharply as the concentration was increased, with the expected concurrent increase in the yield of (2), as illustrated in Table 2.] The acid resin was then filtered off, the filtrate was washed with 2 × 300 cm^3 of 0.25M-aqueous sodium hydrogen carbonate and subsequently dried (Na_2SO_4). The solvent was removed on a rotary evaporator and the residue was distilled at reduced pressure. Two products were collected, the lower-boiling component being the monoacetal (1) and the higher-boiling one the corresponding diacetal (2). Diacetals solidified and were recrystallised from methanol. (They are mixtures of *E*- and *Z*-isomers; no attempt was made to separate these.)

2-Phenyl-, -propyl-, and -isopropyl-8-crown-3 were prepared by adaptation of the method described by Astle *et al.*[10]

The required diols, ethylene- and triethylene-glycol (B.D.H.) anf diethylene- and tetraethylene-glycol (Aldrich) were commercial reagent grade products.

Benzo-2-methyl-5-crown-2 (3; n = 0), benzo-2-methyl-11-crown-4 (3; n = 1) and benzo-2-methyl-17-crown-6 (3; n = 2) were prepared from 1,2-dihydroxybenzene (catechol) and dichloro-compounds as follows. (3; n = 0): Powdered sodium hydroxide (0.21 mol) was added to a solution of catechol (0.1 mol) in dimethyl sulphoxide (200 cm^3). The mixture was warmed to 50 °C and 1,1-dichloroethane (0.12 mol) was slowly added from a dropping funnel. The temperature was raised and the solution refluxed (3 h). Water (200 cm^3) was added to the cooled reaction mixture and the solution was then steam-distilled. The two-phase distillate was cleanly separated by extraction with ether. After being dried (Na_2SO_4), the extract was stripped of solvent on a rotary evaporator, and the residue was distilled under reduced pressure. (3; n = 1 and n = 2): the foregoing general method was modified in the following respects. Butan-1-ol (250 cm^3) was used as solvent, the heating was carried out under nitrogen, and the scale of the experiment was reduced to one-fifth (in molar amounts). The precipitated sodium chloride was filtered off before the solvent was removed on a rotary

Table 3. Yields and analytical data

Compound	B.p. (°C/mmHg)	M.p. (°C) [a]	Yield [b] (%)	Carbon (%)		Hydrogen (%)		Mol. wt.			Acetaldehyde equivalent
				Required	Found	Required	Found	Required	Found [c] A	Found [c] B	
8-C-3	32 (1.0)		29	54.55	54.57	9.10	9.33	132		132	1.03
11-C-4 :	60 (0.20)		5	54.55	54.28	9.10	9.20	176		176	0.97
14-C-5	82 (0.15)		8	54.55	54.13	9.10	9.25	220		220	1.01
17-C-6	120 (0.10)		13	54.55	53.63	9.10	9.27	264	262 ± 4	264	1.03
20-C-7	150 (0.05)		20	54.55	53.98	9.10	8.95	308		308	1.00
Pr-8-C-3	60 (1.0)		26	60.00	59.61	10.00	10.14				
Pr^{i}-8-C-3	56 (3.0)		36	60.00	59.65	10.00	10.08	160		160	
Ph-8-C-3	80 (1.0)		18	68.04	67.89	7.22	7.40				
D-16-C-6		36—37	1.5 [d]	54.55	54.52	9.10	9.03	264	264 ± 4		2.02
D-22-C-8		61—62	4 [d]	54.55	54.70	9.10	9.36	352	346 ± 6		2.05
D-28-C-10		33—34	1 [d]	54.55	54.06	9.10	9.30	440	438 ± 12		1.98
D-34-C-12		52—53.5	1 [d]	54.55	53.81	9.10	9.13	528	536 ± 8		2.04
B-5-C-2	32 (1.0)		23	70.59	70.29	5.88	6.03	136		136	
B-11-C-4		48	19	64.28	63.73	7.14	7.38	224		224	
B-17-C-6		52	17	61.54	61.48	7.69	7.88	312		312	

Compound	B.p. (°C/mmHg)	Yield [b] (%)	Chlorine (%)		Hydrogen (%)		Acetaldehyde equivalent
			Required	Found	Required	Found	
CEEE	126 (0.10)	61	25.82	25.71	7.27	7.10	0.99
CEEEE	162 (0.05)	36	19.56	19.31	7.71	7.91	1.03

[a] Uncorrected. [b] Yield of condensation step (under conditions specified in text). [c] A: Isopiestic vapour pressure osmometry (Hitachi–Perkin Elmer model 115), acetone solvent, extrapolated to zero concentration. 18-Crown-6 was used in calibration runs. (Measurements by Dr. D. S. Baker.) B: Chemical ionisation mass spectrometry. (Measurements by Drs. R. A. Hancock, R. Walder, and H. Weigel, Royal Holloway College.) [d] Yield as by-product in preparation of monoacetal.

evaporator. The product from the final distillation solidified on cooling and was recrystallised from n-heptane.

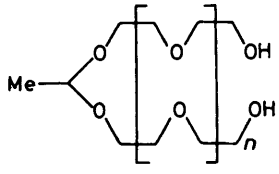
The required dichloro-compounds CEE (4; $n = 0$) and CEEE (4; $n = 1$) were prepared by stirring 2-chloroethanol (0.4 mol) [or 2-(2-chloroethoxy)ethanol, respectively] with acetaldehyde (0.2 mol) in the presence of dried calcium chloride (12 g). Calcium chloride was subsequently filtered off, and the product (filtrate) was distilled under reduced pressure. The same method was found to be equally applicable to the preparation of CEEEE (4; $n = 2$) by starting from 2-[2-(2-chloroethoxy)ethoxy]ethanol. The chloro-alcohols used in these preparations were commercial samples (Aldrich).

Further details of preparations and products are given in Table 3.

Discussion

Because of the inadequate information provided by combustion analysis, other analytical and physical methods were used to characterise the compounds, as will now be discussed.

For a number of the compounds the ' acetaldehyde equivalent ' was determined. This is the number of moles of acetaldehyde produced on hydrolysis of one mole of acetal in dioxan–water (60 : 40, v/v) at 25 °C, using hydrochloric acid as catalyst. The final concentration of acetaldehyde was



(5)

determined spectrophotometrically at the absorption maximum (*ca.* 280 nm). The value of the required molar absorption (extinction) coefficient ($\varepsilon_{max.} = 9.80$) was obtained from the hydrolysis under identical conditions of a pure specimen of 2-methyl-1,3-dioxolan (5-C-2). For monoacetals and diacetals the theoretical values of the acetaldehyde equivalent are 1.00 and 2.00, respectively. Experimental values are given in the final column of Table 3. The purity of successive preparations was monitored by these assays.

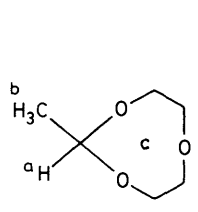
The acetaldehyde equivalent is a good test of purity and affords the clearest distinction between acetals of the cyclic formula (2) and open-chain compounds of formula (5), which are also conceivable by-products in the preparation of (1). Distinction between (2) and (5) is additionally provided by (a) the better agreement of the measured molecular weight

Table 4. 1H N.m.r. spectra of methyl acetals

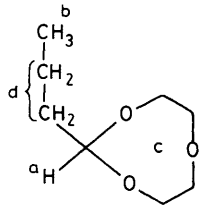
Compound	Signal positions (δ) CH_3CH (a) (All q)	CH_3CH (b) (All d)	Other (c) alicyclic	Aromatic	J_{ab} (Hz)	Integral b/a Calc.	b/a Obs.	c/a Calc.	c/a Obs.
5-C-2	4.97	1.36	3.69—4.09(m)		5.0	3	3	4	4.1
8-C-3	4.81	1.32	3.56—3.99(m)		5.3	3	3	8	8
11-C-4	4.90	1.33	3.59—3.98(m)		5.6	3	2.9	12	12.1
14-C-5	4.83	1.31	3.36—3.98(m)		5.6	3	2.9	16	16.3
17-C-6	4.83	1.32	3.36—4.01(m)		5.3	3	2.9	20	20.5
20-C-7	4.83	1.33	3.32—3.81(m)		5.3	3	3	24	24.3
D-16-C-6	4.83	1.33	3.58—3.97(m)		5.3	3	2.9	8	8.1
D-22-C-8	4.84	1.33	3.69(d) §		5.3	3	2.9	12	12.2
D-28-C-10	4.83	1.33	3.67(s) §		5.3	3	3	16	16.3
D-34-C-12	4.81	1.32	3.65(s) §		5.3	3	2.8	20	20.4
B-5-C-2	6.21	1.66		6.77(s) *	5.0	3	3		
B-11-C-4	5.01	1.38	3.66—4.22(m)	6.88(s) †	5.3	3	3	8	8.2
B-17-C-6	4.86	1.31	3.86—4.20(m)	6.89(s) ‡	5.3	3	3	16	16.4
CEE	4.86	1.36	3.43—3.99(m)		5.3	3	2.9	8	8
CEEE	4.82	1.33	3.37—3.85(m)		5.3	3	2.9	16	16.4
CEEEE	4.80	1.32	3.36—3.98(m)		5.3	3	2.8	24	23.6

* Intensity of aromatic/a: calc., 4; obs. 4.1. † Intensity of aromatic/a: calc., 4; obs. 3.9. ‡ intensity of aromatic/a: calc., 4; obs. 4.1. § Or unresolved multiplet.

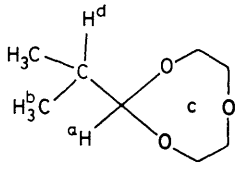
Table 5. ^1H N.m.r. spectra of other 2-substituted 8-crown-3 acetals



8-C-3



Pr-8-C-3



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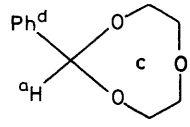

Ph-8-C-3

Compound	Signal positions (multiplicity) a	b	c	d	Integral b/a Calc.	b/a Obs.	c/a Calc.	c/a Obs.	d/a Calc.	d/a Obs.
8-C-3	4.81(q)	1.32(d)	3.56—3.99(m)		3	3	8	8		
Pr-8-C-3	4.59(t)	0.92(t)	3.56—4.03(m)	1.18—1.70(m)	3	3	8	8.1	4	3.9
Pri-8-C-3	4.25(d)	0.91(d)	3.61—4.01(m)	1.62—1.92(m)	6	6.1	8	8.2	1	1
Ph-8-C-3	5.68(s)		3.47—4.11(m)	7.21—7.59(m)			8	8.2	5	5

(Table 3), since compounds (5) are heavier by 26 Daltons, and this difference is outside the experimental error of the isopiestic determination, (b) the absence of ^1H n.m.r. signals ascribable to hydroxy-protons, and (c) the integrals for the CH_3CH protons in relation to those for ring protons in the n.m.r. spectra.

^1H N.m.r. spectra (Bruker *HFX* 90, FT), measured in $CDCl_3$ at 25 °C, of methyl acetals showed mutually split doublet (at *ca.* δ 1.3) and quartet (at *ca.* δ 4.8) signals characteristic of the $CH_3CH=$ grouping. The other protons give rise to a complex signal, at an intermediate frequency, which was not resolved at 90 MHz. For all series the relative intensities of the three groups of signals provide additional analytical information. The data are summarised in Table 4. Other 2-substituted 8-crown-3 acetals gave the proton spectra expected on the basis of the assigned structures (Table 5).

For the members of series (3), the positions of the resonances of the acetal group are displaced by the aromatic

Table 6. Chemical shifts (δ/p.p.m.) in ^{13}C n.m.r. spectra

Compound	CH_3CH	CH_3CH	Other (relative intensity)
5-C-2	19.88	101.68	65.03 (2)
8-C-3	22.11	103.85	69.66 (2), 73.06 (2)
11-C-4	19.41	99.16	63.39 (2), 71.01 (4)
14-C-5	19.47	99.51	64.03 (2), 70.42 (2), 70.72 (2), 71.07 (2)
17-C-6	19.47	99.16	63.86 (2), 70.48 70.60 (6)
20-C-7	19.47	99.04	63.62 (2), 70.37 (2), 70.60 (6), 71.01 (2)

ring current. The associated paramagnetic shift is most marked for the nearest H nucleus (CH_3CH), whereas the effect is much smaller for the more remote CH_3CH nuclei (Table 4). Both shifts are most pronounced for B-5-C-2, perceptible for B-11-C-4, and barely significant for B-17-C-6, as expected in view of the increasing distance of the acetal grouping from the aromatic ring. At the same time, the complex resonance of the protons in the aliphatic ring of the two larger members of the series extends further downfield than for members of series (1) or (2), as expected for the positions marked y (adjacent to the catechol oxygen atoms) in formula (3).

^{13}C N.m.r. spectra (proton-decoupled) of series (1) were measured at a high concentration (*ca.* 50% v/v) in $CDCl_3$ (Table 6). The chemical shifts exhibit a fairly regular pattern, consistent with the formulae, with the highly strained compound 8-C-3 showing a consistent downfield displacement of all signals. For comparison, the corresponding signal positions for acetaldehyde are at δ 30.84 and 199.84.

The kinetics of hydrolysis of the 2-methyl-(3*n* + 5)-crown-(*n* + 2) group of acetals are reported in some detail in another paper.[5] Rates of hydrolysis of other acetals catalysed by hydrochloric acid, are summarised in Table 7. They were followed as rates of formation of acetaldehyde.

Because the liberation of acetaldehyde from diacetals occurs in two successive stages, the hydrolysis of these compounds does not obey first-order kinetics. The quoted second-order rate coefficient for a typical member of the series is intended only as an approximate indication of the stability of the substrates in acidic media.

For the open-chain acetals CEEE and CEEEE, the observed first-order rate constants were accurately proportional to acid concentrations. For the less reactive compound CEE higher acid concentrations were used, and the second-order rate coefficient increased with concentration by a factor of 1.5 over the range 0.04—0.24M-hydrochloric acid and is interpreted as an electrolyte effect. The addition of metal chlorides to the dilute acid had a qualitatively similar effect on the rate of hydrolysis of all three acetals. It did not provide evidence of cation-binding. The rate constant given in Table 7 refers to the limiting value at low acid concentration. The increase in reactivity with chain length is consistent with the decrease in the inductive effect of the chlorine atoms (which reduces the basicity of the acetal oxygen atoms).

Table 7. Rates of hydrolysis at 25 °C

Compound	$10^3 \times k_2$ ($dm^3\ mol^{-1}\ s^{-1}$)	Solvent
CEE	2.4	60 :40 (v/v) Dioxan–water
CEEE	15.0	60 :40 (v/v) Dioxan–water
CEEEE	24.8	60 :40 (v/v) Dioxan–water
Pr-8-C-3	600	Water
D-22-C-8	40	40 :60 (v/v) Dioxan–water

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