Tetrahedron Vol 45, No 7, pp 2201 to 2212, 1989
Printed in Great Britain

0040-4020/89 $3 00+ 00

TEMPLATE EFFECTS. 7.[1] LARGE UNSUBSTITUTED CROWN ETHERS FROM POLYETHYLENE GLYCOLS: FORMATION, ANALYSIS, AND PURIFICATION

Chiara Antonini Vitali and Bernardo Masci*

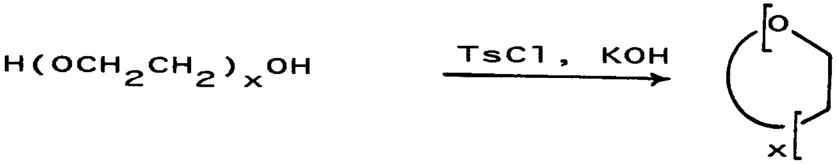
Dipartimento di Chimica and Centro C.N.R. di Studio sui Meccanismi di Reazione,
Università di Roma "La Sapienza", P.le Aldo Moro 2, 00185 Roma, Italy.

(*Received in UK* 26 *January* 1989)

Abstract - Through the reaction of polyethylene glycols with tosyl chloride and heterogeneous KOH in dioxane not only coronands from [12]crown-4 to [24]crown-8 can be obtained but also some larger homologues. A systematic investigation has shown that: i) [27]crown-9 and [30]crown-10 can be formed from nona- and deca-ethylene glycol, respectively, and isolated in pure form; ii) the whole series of polyethylene glycols from tri- to deca-ethylene glycol yields not only the corresponding crown ethers but also higher cyclooligomers that can be analyzed up to about [60]crown-20 by glc: in particular [36]crown-12 and [48]crown-16 were obtained from tetraethylene glycol and purified by column chromatography on cellulose; iii) the reaction, as applied to commercial mixtures of polyethylene glycols (from PEG 200 to PEG 1000), gives fairly high yields of crown ethers also in the region of large ring sizes. The contribution of the template effect of K^+ ion and the cyclooligomerization reactions for the various ring sizes are discussed.

The template effect of alkali metal ions in the formation of coronands can be thought to occur both by bringing together two reactive molecules and by bringing "closer" the chain termini in the cyclization step. So far no more than some suggestive drawings support the former catalytic mechanism , which can be called intermolecular template effect, whilst the latter (intramolecular template effect) is a well established one.[1-4] Template effects are reported to operate also in the formation of large coronands,[1,5,6] but the subject has not yet been investigated in a systematic way: in particular the formation of structurally simple compounds, such as unsubstituted crown ethers (UCE) should be investigated to get information on the role that the template effect can play in the formation of large macrocycles.

Generally, UCE are prepared in the laboratory by Williamson etherification reactions,[2] either by reacting a polyethylene glycol (PEG) with a PEG derivative, such as a ditosylate, in the presence of a base, or by reacting a PEG, which already has the required number of oxyethylene units, with arenesulfonyl chlorides and heterogeneous KOH or NaOH. The latter one-pot method (eq 1), first reported by Okahara et al.,[7] is known to be suitable for the



1)

preparation of UCE from 15C5 to 24C8:[8] clearly the preparation of the starting long chain PEG is required by this approach. The preparation of pure samples of PEG and UCE with more than six oxyethylene units is not a trivial task. Purification by fractional distillation is more and more difficult on increasing the molecular weight; moreover we observed that significant amounts of close homologues are usually formed besides the desired compounds in both the cyclic and the open chain series, although pure monodisperse precursors are used. Then the use of an efficient chromatographic analysis seems to be compulsory whenever monodisperse UCE and PEG are required: we found that glc is a suitable analytical tool for quite large compounds in both series. We report in this paper on the formation of UCE in a wide range of ring sizes through the Okahara reaction: the systematic use of glc allowed several new features of the reaction to be observed, mostly connected with the formation of large UCE.

Our aims were: i) to find the conditions for properly working with fairly large PEG and UCE, ii) to widen the scope of the Okahara reaction, and iii) to obtain information on the relative ease of ring formation in the presence of a templating agent over a wide range of ring sizes.

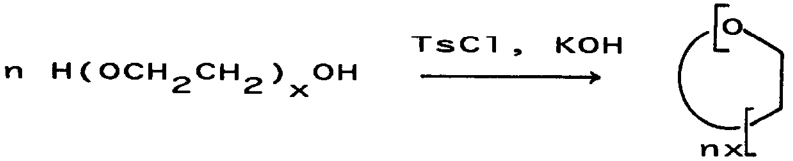
RESULTS

We did not optimize the yields of the reactions but worked in conditions that allowed reproducibility of the results. KOH was in all cases the condensing and templating agent, dioxane the solvent, TsCl the arenesulfonyl chloride and 65 ± 3 °C the temperature.

Preparation of 27C9 and 30C10 from long chain PEG. The syntheses of nona- and decaethylene glycol, and of the corresponding UCE according to eq 1, were readily carried out, but fractional distillation could not effectively purify the obtained glycols and coronands from unexpected close homologues which were revealed by glc. The final purification was carried out by recrystallization at low temperature for the two PEG and for 30C10, and by a partition chromatography technique on cellulose for for 27C9. Interestingly continuous extractions can be used instead of thermal decomposition of the complex: these turned out to be particularly valuable in the preparation of larger UCE which cannot be distilled.

The formation and isolation of large UCE from short chain PEG. Okahara reported[7] that on attempted preparation of 12C4 from tetraethylene glycol in the presence of NaOH, much more 24C8 than 12C4 was obtained , and that only 18C6 was obtained from triethylene glycol in the presence of KOH.

On refining the glc analysis a much wider picture is apparent, namely not only "dimeric" cycles but also larger cyclic oligomers are formed: moreover the formation of cyclic oligomers is not limited to the reaction of tri- and tetra- ethylene glycols, but occurs quite generally. On its hand the "monomer" which undergoes cyclooligomerization is obtained by oligomerization of ethylene oxide , and the reaction can be viewed as a discrete increase in the degree of polymerization of ethylene oxide (eq 2).



2)

A complete picture of the various cyclooligomerization reactions observed is given in Table 1 for the whole series of starting PEG, from triethylene glycol to decaethylene glycol, reacted in strictly the same conditions. Our analytical technique allowed UCE up to 63C21 to be detected, but values for UCE higher than 48C16 are less reliable than the others.

The values arrayed in the table give several pieces of information: yields of the various UCE as obtained from a given precursor (vertical lines); yields of a given UCE as obtained from different precursors (horizontal lines); yields of the various UCE corresponding to n = 1 in eq 2 (upper transversal line) and to n = 2, 3, etc... (following transversal lines in the order). In all cases but for x = 3 and 4, the highest yield of a given UCE is obtained with n = 1. All the products expected from a mathematical point of view have been observed to form: the yields are very low in some cases, but at least in principle a number of fairly large UCE can be obtained by this very simple approach.

Actually , starting from the commercially available tetraethylene glycol we could isolate 36C12 and 48C16 in pure form, besides 12C4 and 24C8. Through our chromatographic technique on cellulose 36C12 and 48C16 could also be separated from the small but significant quantities of close homologues which formed, in this as in the other cases, besides the products expected on the basis of eq 2. The "pentameric" 60C20 was also obtained, although contaminated by its close lower homologues.

Table 1: Yields % of the Cyclooligomerization Reactions of Polyethylene Glycols According to the Reaction $n\ \mathrm{H(OCH_2CH_2)_xOH} \longrightarrow \left\lfloor\overline{\mathrm{(OCH_2CH_2)}}\right\rfloor_{nx} \equiv \mathrm{3nxCnx}$.[a]

x	3	4	5	6	7	8	9	10
UCE 3nxCnx								
9C3	-[b]							
12C4		1.4						
15C5			46					
18C6	42			69				
21C7					60			
24C8		23				36		
27C9	10						44	
30C10			12					43
33C11[c]								
36C12	4.1	11		1.1				
39C13[c]								
42C14					4.4			
45C15	2.2		3.4					
48C16		4.3				7.6		
51C17[c]								
54C18	2.0			0.1			5.0	
57C19[c]								
60C20		1.2	0.7					1.4
63C21	1.3				1.5			

(a) In the presence of TsCl and KOH in dioxane at 65 °C. (b) The very low yields of 9C3 could not be exactly determined. (c) These UCE are considered in order to save the regularity of the array: obviously, according to eq 2, whenever nx is a prime number the corresponding UCE can only be obtained from cyclization of the "monomeric" PEG (for $x \neq 1$).

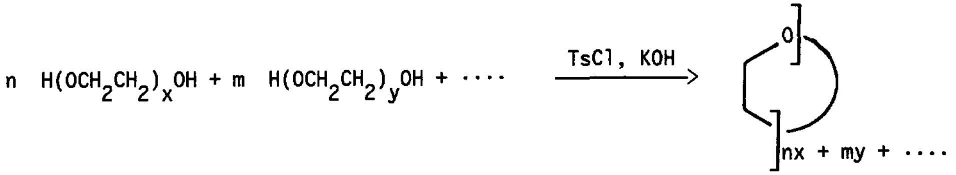
<u>glc Analysis</u>. The preparation of pure samples of a number of UCE allowed a quantitative analysis to be carried out on the whole series up to about 60C20. Regular trends were obtained both in the retention times under isothermal conditions and in the response factors by flame ionization detection, so that also the homologues which were not

available as pure compounds could be identified and quantitatively determined in the reaction products. The response factors for UCE larger than 48C16 were obtained by extrapolation, but a break in the observed regular trend is likely to occur somewhere between 48C16 and 60C20, as higher UCE, which very likely are also formed, are not easily detected by glc. The actual amounts of UCE larger than 48C16 are likely to have been underestimated.

The UCE formation from commercial mixtures of PEG. The reaction on commercial mixtures of PEG is a promising route to obtain UCE, as polyoxyethylene chains of all the desired lengths can be found in these cheap materials. It is an alternative to the direct preparation of mixtures of UCE through cationic polymerization of ethylene oxide, which has been carried out in the presence and in the absence of templating agents.[9,10] As cationic polymerization is reversible, equilibrium products are finally obtained (dioxane or small UCE), whilst through the Williamson reaction no such limit holds. We had previously prepared UCE from PEG 300 by bromination followed by reaction with $Ba(OH)_2$ in water,[11] and Okahara carried out his reaction on PEG 200:[7] crown ethers up to 24C8 were observed to form. Also in this case improvements in glc analysis allowed a much wider picture to be observed. PEG 200, 300, 400, 600, and 1000 were reacted in the same conditions with KOH and TsCl in dioxane: from the glc analysis the composition of the reacted mixture could be determined. UCE as large as 72C24 could be detected but also in this case the data for UCE larger than 48C16 are probably underestimated: in particular the data for PEG 1000 seem to be of limited reliability.

In the case of PEG 200, 300, and 400 a glc analysis of the starting mixtures could be carried out, so that a direct comparison can be made with the UCE composition in the reaction products. The results are presented in a compact form in Fig. 1 as the mg of the various oligomers in 1 g of the commercial mixtures of PEG, and the mg of the various UCE obtained from that amount of material. The total amounts of UCE obtained from 1 g of the various PEG mixtures are as follows: PEG 200, 490 mg;PEG 300, 600 mg; PEG 400, 390 mg; PEG 600, 300 mg; PEG 1000, 75 mg (underestimated).

Fig. 1 shows that large UCE are formed even from PEG 200, which has octaethylene glycol as the largest detected component: they are clearly produced by the union of smaller fragments followed by cyclization, according to the general eq 3, which is an extension of eq 2. In the case of PEG 200 the oligomer distribution in the final products is significantly different from that in the starting material: in the other cases, apart from the long tail of high molecular weight products, fairly small differences are observed, and the values of the yields reported in the upper transversal line in Table 1 account for



3)

many of them. Namely the largest amount of detected UCE appears to be produced by the union of smaller fragments in the case of PEG 200, and by direct cyclization of the corresponding "monomeric" chains in the other cases.

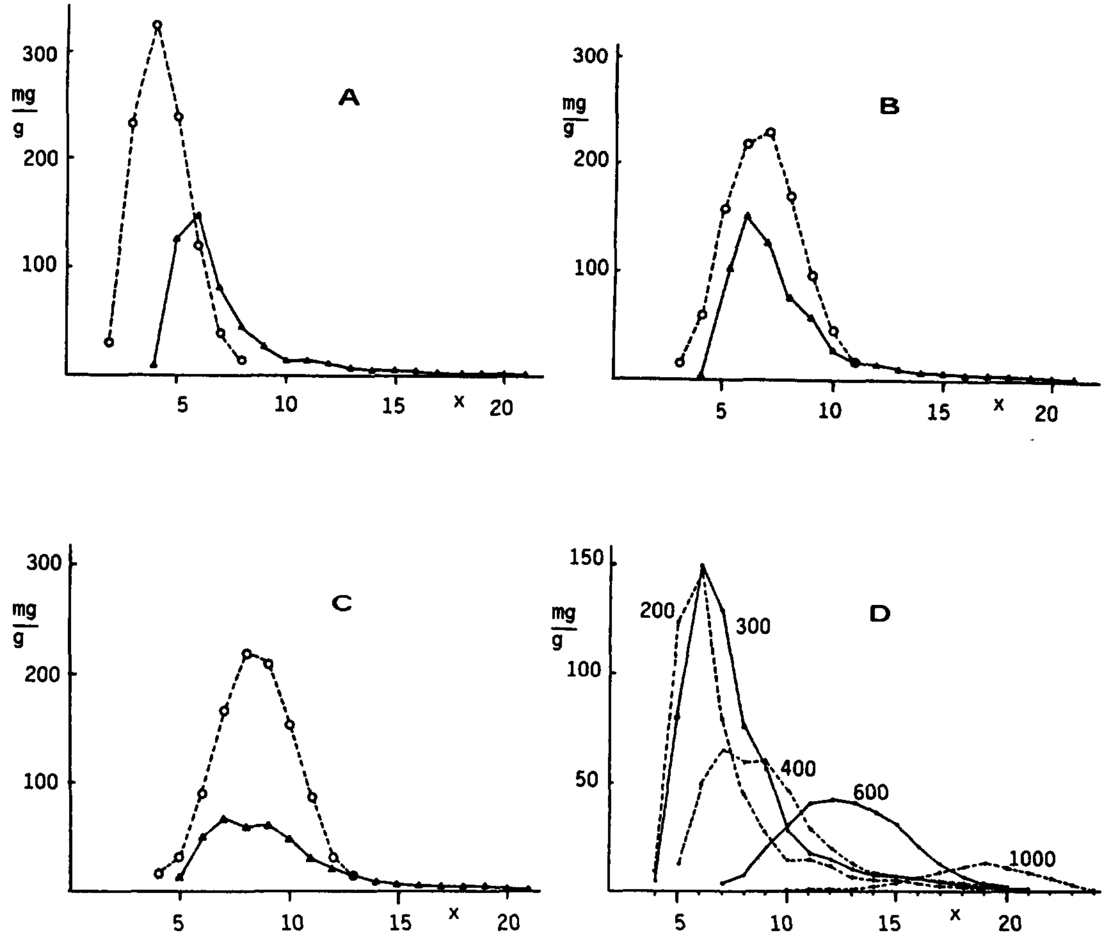


Fig. 1. A) mg of $HO(CH_2CH_2O)_xH$ (○) in 1 g of PEG 200 and mg of $\lfloor(OCH_2CH_2)_x\rfloor$ (▲) obtained from 1 g of PEG 200. B) The same for PEG 300. C) The same for PEG 400. D) mg of $\lfloor(OCH_2CH_2)_x\rfloor$ obtained from 1 g of PEG 200, 300, 400, 600, and 1000.

DISCUSSION

Not only K^+ ion directs the reaction of monodisperse or polydisperse PEG towards UCE of complementary size, but also allows the formation of the whole family of compounds from 12C4 to 72C24 (and presumably beyond 72C24). This can be due to several reasons. First of all the directing action of the template is not expected to be a rigid one but to operate, with varying effectiveness, in a range of ring sizes, moreover it may happen that more than one cation enters the cavity of the cyclic transition state. In order to carry out a deeper analysis on the whole observed picture the multifarious role of K^+ ion must be reckoned with, namely it can: i) increase the acidity of the starting PEG and of the intermediate $H(OCH_2CH_2)_xOTs$ derivatives by complexing the anionic forms better than the neutral ones;[12] ii) affect the nucleophilicity of the various anionic species through ion pairing;[3] iii) modify the rate and possibly the products of the heterogeneous reaction by increasing the concentration in the liquid phase of OH^- which is the counterion of the complexed K^+ ion; iv) increase the proximity of the chain termini, that is the tendency to ring closure. Strictly this last action is the template effect and must be specially sensitive to the geometrical complementarity between the cation and the formed ring.[1] The other actions are probably smooth monotonous functions of the number of oxygen atoms: they can turn out to be very important to allow the Williamson reaction to take place, but are not likely to influence the cyclization tendency with respect to polymerization.

Let's consider two limiting cases: when the chain length is the right one for the metal ion template, fast cyclization should suppress polymerization and minimize the formation of other by-products. On the other hand the above actions i-iii of K^+ on a very long polyoxyethylene structure could still prevent hydrolytic reactions from suppressing the desired etherification reactions, but the cyclization step should not take any advantage over polymerization. Then, in the latter limiting case, even without appealing to the intervention of more than one cation in the transition state, the influence of the "small" K^+ ion should be significant[13] but the distribution of the various cyclic oligomers should be ruled by the general laws of cyclooligomerization of bifunctional substrates[14,15] and not by the template effect. Clearly, the actual systems are in intermediate situations, with a gradual shifting from a strict control by the template, as in the reaction of hexaethylene glycol, to the looser control which apparently operates on the reactions of very long chains. The vertical trends in Table 1 can be interpreted as the normal trends for cyclooligomer formation from bifunctional compounds, to which a more or less strong perturbation, caused by the template effect, is superposed. Although the theory of cyclooligomerization reactions is well developed[14,15] there seems to be no chance to calculate the expected distribution in the absence of the template effect for our heterogeneous and multistep reactions under influx conditions.

The formation of cyclooligomers starting from triethylene glycol deserves a further comment, which should apply also to other cases. Clearly K^+ does not act as an effective template for the formation of the relatively small "monomeric" cycle 9C3: dimerization can take place and templated cyclization to the "dimeric" cycle follows. However in this case the formation of 18C6 is not so markedly favoured with respect to higher cyclic oligomers as in the case of the reaction from hexaethylene glycol. This is probably due to the fact that in the case of hexaethylene glycol the "monomer" added to the reacting mixture is quickly removed by the templated cyclization and the steady concentration of $Ts(OCH_2CH_2)_6OH$ (and species in equilibrium with it) is low; when triethylene glycol is the starting material, the steady concentration of $Ts(OCH_2CH_2)_3OH$ is very likely to be higher and the intermediate "dimeric" chain $H(OCH_2CH_2)_6O^-$ has more opportunity to react with it before being converted to $H(OCH_2CH_2)_6OTs$.

The overall picture in Fig. 1D indicates that the yields for the cyclization of "monomeric" precursors decrease on increasing the chain length, as expected for the cyclization of bifunctional precursors[16] even in the absence of template effects. Actually the decrease appears to be too smooth when allowance is made for the strong template effect that must operate in the formation of 18C6 and close homologues: the yields for the overall conversion are about 60% from PEG 300 and about 30% for PEG 600. Then template effects are likely to operate also in the formation of large coronands and the involvment of more than one cation in the cavity of the large cyclic transition state can be suggested [1,6] to account for the high yields obtained. Nevertheless the complexity of the reaction must be taken into account, namely a series of steps precede the ring closure also in the cyclization from the "monomeric" glycol, and a levelling of the yields can be partly due to those steps or to side reactions.

The possible template effect by two cations will be dealt with more specifically in the following paper.

CONCLUDING REMARKS

The formation of cyclooligomers larger than the desired coronand in spite of the operation of the template effect has been observed in some circumstances, in particular in the investigation of Reinhoudt et al..[5] Actually, the formation of higher cyclooligomers can be thought to occur in all macrocyclization reactions in preparative conditions, and the purification technique of the desired product must distinguish between them. In the formation of UCE (as well as in the formation of the corresponding open chain PEG) a further complication is represented by the formation of close homologues which accompany the formation of both the "monomeric" and the "oligomeric" cycles. The amount of these materials is small, but significant, when compared to that of the expected close homologues, and can contaminate the products. We shall investigate in more detail the formation of these side products and check their formation with other preparation methods of large UCE. According to the only previous report on the subject, large UCE were prepared from a PEG, a polyethylene glycol ditosylate and NaH or KH, and purified by column chromatography on alumina:[6] no comment is found in that report on the presence of contaminating homologues, but no chromatographic analysis appears to have been carried out. We also point out that in our hands column chromatography on alumina was ineffective to separate the various UCE, and that the melting points of large UCE prepared by us are significantly higher than those reported in that paper.

Although glc has obvious limits in the analysis of such high boiling compounds, it allows a quantitative analysis. Actually , this is quite delicate and time consuming, but we think that at least a qualitative use of this technique should be recommended as a rapid and sensitive tool to check the purity (in particular the monodispersity) of even large polyoxyethylene compounds.

EXPERIMENTAL

NMR spectra were taken on a Bruker WP80SY Spectrometer in $CDCl_3$ solution. The mass spectra were recorded on a Kratos MS 80 spectrometer: by electron impact all the isolated UCE gave the expected M^+ (amplified). The following chemicals were used as received: triethylene glycol and toluene-4-sulfonyl chloride (Erba); 1,2-bis(2-chloroethoxy)ethane, powdered KOH, 12C4, 15C5, PEG 200, 300, 600, and 1000 (Fluka), PEG 400 (Merck); tetraethylene glycol (Aldrich). 18C6 (Fluka) was distilled under vacuum.

Polyethylene glycols - Nonaethylene glycol was prepared, according to Krespan,[17] from triethylene glycol dichloride (0.6 mol), NaOH, and excess triethylene glycol. Fractional distillation under vacuum gave the desired product with a purity from 91 to 97% in the various fractions, close homologues being the contaminating products: the overall yield was 28%. The less pure fractions could be purified by recrystallization at -20 °C from CCl_4: the product filtered under an argon atmosphere was 99% pure by glc. The above procedure was extended to the preparation of decaethylene glycol from tetraethylene glycol dichloride (prepared according to Pedersen[18]), NaOH and excess triethylene glycol. The recrystallized product was obtained in 23% yield (98.5%

purity). Penta-, hexa-, hepta-, and octa-ethylene glycol were available from previous investigations[19,20] and further purified by fractional distillation when necessary. The homologues from hepta- to deca-ethylene glycol used for the systematic investigation had the following melting points: hepta-, 17.8-18.8 °C; octa-, 19.7-21.8 °C; nona-, 24.0-25.2 °C; deca-, 25.8-28.3 °C. In the literature they are reported to be oils, except for the very careful preparation by Bömer et al.[21] (mp 29.8-30.0 °C for nonaethylene glycol).

27C9. 25 mL of a solution of nonaethylene glycol (4.13 g, 10.0 mmol) and TsCl (1.9 g, 10.0 mmol) in dioxane were added over 100' to a suspension of powdered KOH in 60 mL of dioxane stirred and heated at 65 °C. In order to obtain regular and reproducible rate of feed, the addition was carried out by means of a syrynge operated by a Sage Instruments syrynge pump 355. Stirring and heating were continued for additional 7 h, the cooled mixture was filtered and the solid repeatedly washed with CH_2Cl_2. The residue obtained from the combined liquid phases (4.0 g) was dissolved in $CHCl_3$ and used for the analytical determinations: on a portion (59%) the isolation of the "monomeric" UCE was carried out. After a continuous extraction of the crude product with hexane (15 h) 0.97 g of 27C9 were isolated (91% purity, about 38% yield) and further purified by elution with benzene on a cellulose powder column (Whatman CF11) which had been treated with n-BuOH saturated with water. An oil was obtained with 98% purity by glc, ^1H NMR (δ) 3.65, s.

UCE of various ring sizes from monodisperse PEG. The same molar quantities, the same reaction conditions and the same work-up procedure as reported for the preparation of 27C9 were used for the whole family of PEG, from tri- to decaethylene glycol: the $CHCl_3$ solutions were used for the glc analysis of the cyclooligomers (data in Table 1). The purification by continuous extraction and partition chromatography was used to obtain pure samples (>98.5%) of 21C7 and 24C8 for analytical purposes.

The reaction on commercial mixtures of PEG. Exactly the same conditions as reported for monodisperse PEG were used: the weight amounts of PEG 200, 300, 400, 600, and 1000 reacted with 0.02 mol of TsCl were 4.00, 6.00, 8.00, 12.00, and 20.00 g, respectively. In order to allow the glc analysis to be carried out, the crude products from PEG 1000 had to be continuously extracted with hexane (25 h: some loss of material may have occurred).

36C12, 48C16, and 60C20. The reaction on tetraethylene glycol was also carried out on a larger scale (100 g), in order to isolate the higher cyclooligomers. The crude product was distilled under vacuum and several fractions collected up to bp 230 °C (0.01 mm Hg) but the presence of close homologues (mostly 21C7 contaminating 24C8, and 33C11 contaminating 36C12) did not allow pure compounds to be obtained. The residue of the distillation was extracted with several portions of light petroleum/CCl_4 1:1 and chromatographed on column. After unsuccessful attempts on neutral alumina, pure samples (>98.5% by glc), of crystalline 36C12 and 48C16 could be obtained by the aforementioned partition technique on cellulose (elution with benzene): the obtained sample of 60C20 was impure of its lower homologues (85% purity). 36C12 and 48C16 were dissolved in light petroleum, dried over Na_2SO_4 and recrystallized at -20 °C; 36C12: mp 36.5-38.5 °C, lit.[6] oil; 48C16: mp 49.5-50.5 °C, lit.[6] 40-43 °C.

30C10. In a larger scale preparation, decaethylene glycol (15.0 g, 0.0328 mol) and TsCl (6.25 g, 0.0328 mol) in 30 mL of dioxane were added over 7 h to a suspension of powdered KOH (10 g, 0.15 mol) in 200 mL of dioxane heated at 65 °C and reacted for additional 5 h. After the usual work-up, a portion of the crude material (20%, 2.9 g) was continuously extracted with benzene from water: the product extracted in the first 3 h was discarded, and the material extracted in the following 20 h recovered (about

88% pure in 30C10). The product was dissolved in hexane, dried (Na_2SO_4) and recrystallized at -20 °C: 0.9 g, 98% purity, 29% yield, mp 33.5-38 °C.

The other portion of the crude material was distilled under vacuum and the purest fraction (bp 210 °C at 0.1 mm Hg) extracted with light petroleum and recrystallized from light petroleum/CCl_4 at -20 °C (0.9 g, 99% purity, mp 35.5-36.8 °C, lit.[6] oil).

The glc analysis. The analyses were performed on either a Hewlett-Packard 5830A gas chromatograph equipped with a 18850 A terminal or a Varian Vista 6000 apparatus equipped with a Hewlett-Packard 3390A integrator. Detection was by flame ionization and the injection temperature was 400 °C. The most useful columns were as follows: a) 1 m x 1/8 in. glass column packed within 3% OV 17 on 80-100 Supelcoport; b) 1 m x 1/8 in. stainless steel column packed with 5% OV 101 on 100-120 Chromosorb; c) 20 in. x 1/8 in. stainless steel column packed with 10% UCW 982 on WAW Chromosorb 80-100; columns a and b could be operated up to 350 °C.

In all cases pure samples of UCE were used as standard compounds. The conditions for the quantitative analysis were changed until reproducible results were obtained. In ideal conditions the same response is expected for the same weight amount of material if cyclooligomers are analyzed by a flame ionization detector: the actual response factors for our high boiling coronands in typical and reproducible conditions were as reported in Fig. 2. The response factors for UCE compositions similar to those found in the reaction mixtures were determined as necessary.

The retention times in isothermal conditions for the various UCE are reported in Fig. 3: the retention times of the solvent was negligible in the conditions used (flow 20-25 mL/min, column a).

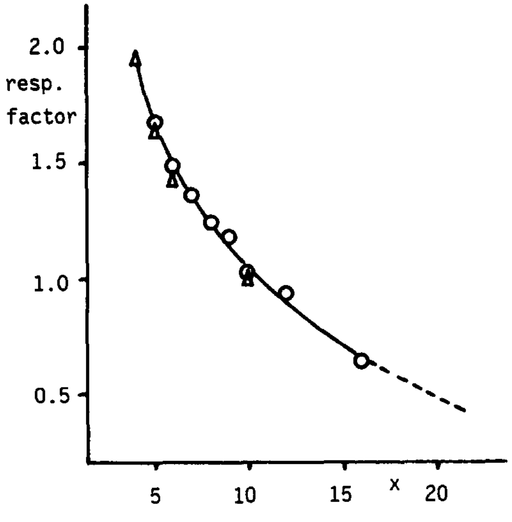


Fig. 2. Response factors for UCE, 3xCx, relative to 30010: values from mixtures containing the same weight amounts of the homologues, obtained using column a (O), and column c (Δ).

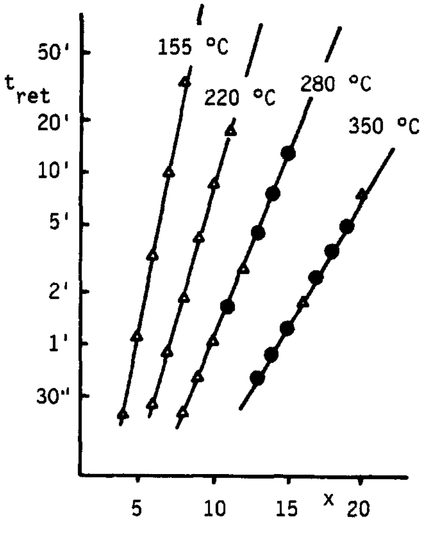


Fig. 3. Retention times under isothermal conditions for UCE, 3xCx: available UCE (▲); UCE identified in the mixtures (●).

The picture for the analysis of PEG was similar but only homologues up to tetradecaethylene glycol could be detected and the results were somewhat less reproducible.

Acknowledgments - Financial support by the Ministero della Pubblica Istruzione is acknowledged. Thanks are due to Prof. L. Mandolini for critically reading the manuscript.

REFERENCES AND NOTES

1) Mandolini, L.; Masci, B. J. Am. Chem. Soc. 1984, 106, 168-174. See also ibid., p. 3706.
2) As a general account see: Gokel, G. W.; Korzeniowski, S. H. "Macrocyclic Polyether Syntheses"; Springer-Verlag: Berlin, 1982.
3) Illuminati, G.; Mandolini, L.; Masci, B. J. Am. Chem. Soc. 1983, 105, 555-563.
4) Mandolini, L. Pure Appl. Chem. 1986, 58, 1485-1492.
5) Reinhoudt, D. N.; Gray, R. T.; Smit, C. J.; Veenstra, I. Tetrahedron 1976, 32, 1161-1169.
6) Chenevert, R.; D'Astous, L. J. Heterocycl. Chem. 1986, 23, 1785-1787.
7) Kuo, P. L.; Kawamura, N.; Miki, M.; Okahara, M. Bull.Chem. Soc. Jpn. 1980, 53, 1689-1693, and references therein.
8) The shorthand notations 15C5, 24C8 etc. will be used throughout this paper to indicate [15]crown-5, [24]crown-8 etc.
9) Kobayashi, S.; Kobayashi T.; Saegusa, T. Polym.J. 1983, 15, 883-889.
10) (a) Dale,J.; Daasvatn. K. J.Chem. Soc. Chem. Commun. 1976, 295-296.
(b) Dale, J.; Daasvatn, K. Acta Chem. Scand. B. 1980, 34, 327-342.
11) Mandolini, L.; Masci, B. Synth. Commun. 1979, 9, 851-856.
12) Ercolani, G.; Mandolini, L; Masci, B. J. Am. Chem. Soc. 1981, 103, 7484-7489.
13) Interestingly, we could not observe the formation of significant amounts of UCE from PEG 600 when $Me_4NOH\cdot 5H_2O$ was used in the place of KOH.
14) For a general account see : "Cyclic Polymers", Semlyen, J. A. Ed.; Elsevier: London, 1986.
15) Ercolani, G.; Mandolini, L.; Mencarelli, P. Macromolecules, 1988, 21, 1241-1246.
16) Mandolini, L. Adv. Phys. Org. Chem. 1986, 22, 1-111.
17) Krespan, C. G. J. Org. Chem. 1974, 39, 2351-2355.
18) Pedersen, C. J. J. Am. Chem. Soc. 1967, 89, 7017-7036.
19) Illuminati, G.; Mandolini,L.; Masci, B. J. Am. Chem. Soc. 1981, 103, 4142-4145.
20) Masci, B. J. Org. Chem. 1985, 50, 4081-4087.
21) Bömer, B.; Heitz, W. Kern,W. J. Chromatog. 1970, 53, 51-54.