

**CAPTODATIVE SUBSTITUENT EFFECTS - PART XXII<sup>1</sup>**  
**RADICAL DEHYDRODIMERISATION AND BRIDGED DEHYDRODIMERISATION**  
**OF MACROCYCLIC POLYETHERS**

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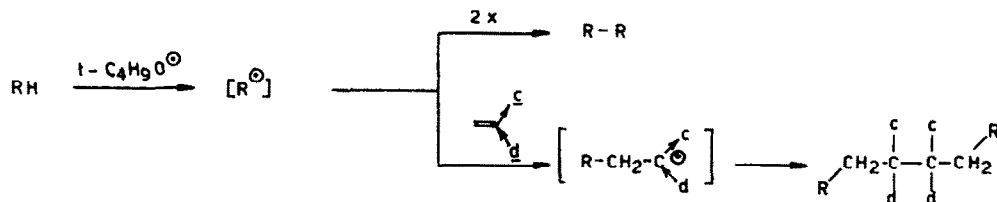
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(Received in UK 4 July 1984)

**Abstract :** Crown ethers are dehydrodimerized in good yields when treated with di-tert.-butyl peroxide in UV light. Bridged dehydrodimers of crown ethers are obtained in the presence of  $\alpha$ -tert.-butylmercaptoacrylonitrile. Cation extraction study was performed in order to compare the binding properties of dehydrodimers vs. monomers.

**INTRODUCTION**

There is an increasing number of ligands which contain two or more macrocyclic moieties and such compounds are often characterized by very strong and/or unusual complexing properties<sup>2,3</sup>. With this in mind, we have applied radical coupling to link two crown ethers together either directly via dehydrodimerisation or by inserting a four carbon atoms bridge through bridged dehydrodimerisation. Radical dehydrodimerisation (DHD)<sup>4,5,8</sup> and bridged dehydrodimerisation (BDHD)<sup>6,7,9</sup> processes have already been successfully applied to a plethora of compounds including alkanes, amines, amides, ethers, alcohols, thioethers, ketones, nitriles and aldehydes.



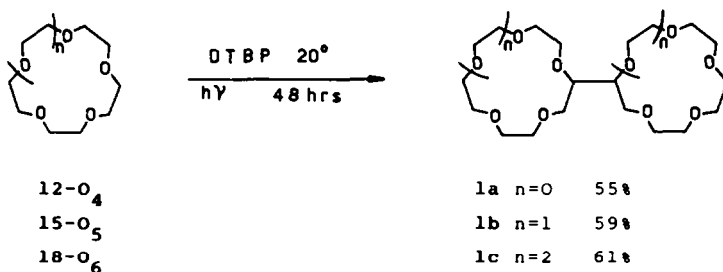
Scheme 1

The BDHD method uses captodative (cd) olefins which efficiently trap the radicals  $R^\bullet$  formed from the substrates RH. The intermediary cd radical adducts can be observed by ESR<sup>10</sup> and they dimerize to adduct dimers. The formation of dehydrodimers is completely absent under such conditions. The overall result amounts to an insertion of a four carbon unit between two radicals of the substrate RH.

## DEHYDRODIMERISATION

The smooth DHD<sup>5</sup> and BDHD<sup>7</sup> of dioxane, which may be considered as the first member of the crown ether family, provided the impetus for the extension of these techniques to 12-O<sub>4</sub>, 15-O<sub>5</sub> and 18-O<sub>6</sub> crown ethers.

Unlike with dioxane, however, the attempts to dehydrodimerize crown ethers using di-tert.-butylperoxide (DTBP) at 140° without any solvent invariably led to complex mixtures including low amounts of desired dimers. The use of di-tert.-butyl peroxalate DTPO, at 60°, equally in twenty fold excess of crown ether did not reveal any improvement. Further attempts using photochemical decomposition of DTBP at 20° in benzene have successfully culminated in the synthesis of dehydrodimers 1a-c. The crown ethers have to be used in about 20:1 molar excess with respect to DTBP. Stoichiometric ratio of reactants results in a substantial decrease in yields of 1a-c, which are then accompanied by oligomers of crown ethers. Low yields of trimers of crown ethers as isomeric mixtures could be isolated from the residues of distillation.

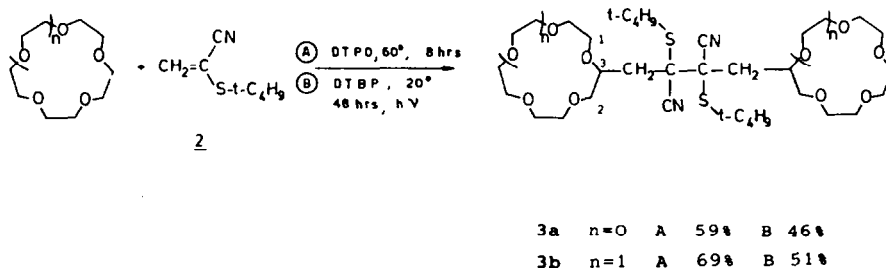


Scheme 2

These new dimers 1a-c consist of a 1:1 mixture of meso and d,l forms<sup>11,12</sup>. Radicals deriving from the 18-O<sub>6</sub> crown ether have been postulated as arising from peroxydisulfate decomposition in the presence of this crown ether. They supposedly decay by a recombination with SO<sub>4</sub><sup>•-</sup> radical-ions rather than by dimerisation<sup>13</sup>. 18-O<sub>6</sub> derived radicals are also involved in photochemical reactions with carbonyl compounds, but the yields are rather low<sup>14</sup>.

## BRIDGED DEHYDRODIMERISATION

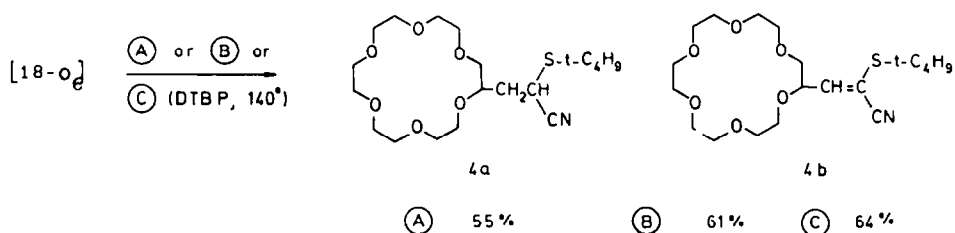
When the hydrogen abstraction is performed photochemically in the presence of  $\alpha$ -tert.-butylthioacrylonitrile 2, the bridged dehydrodimerisation takes place to furnish the corresponding adduct-dimers 3a,b. Even higher yields can be obtained when di-tert.-butyl peroxalate DTPO is decomposed in neat crown ethers at 60°.



Scheme 3

It should be noted that the four carbon bridge carries four functional groups which might be susceptible to various modifications. Till now, bridging of crown ethers was effected solely through functional groups already present at the benzene ring in benzocrown ethers <sup>15,16</sup>.

Bridged dimers **3a,b** dissociate back to corresponding radical adducts upon heating, which ultimately leads to dismutation products **4a,b**. This also implies that overheating must be avoided during the removal of excess starting crown ethers by bulb-to-bulb distillation. It is therefore not surprising that in the case of the highest boiling **18-O<sub>6</sub>** crown ether only dismutation products are obtained.



Scheme 4

The yields given refer to the mixture of **4a** and **4b**. The saturated product **4a** consists of a mixture of diastereomers and the olefin **4b** contains both the geometrical isomers E and Z. Expectedly, using DTBP at 140°, analogous dismuted products (**5ab** and **6ab**) are also obtained with **12-O<sub>4</sub>** and **15-O<sub>5</sub>** crown ethers in 51 and 48 % yields, respectively.

#### CATION EXTRACTION PROPERTIES OF DIMERS **1b** and **1c** vs MONOMERS

Extraction of picrates of alkali metal cations ( $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ) with **1b** and **1c** and the corresponding monomers **15-O<sub>5</sub>**, **18-O<sub>6</sub>** was compared for different concentrations in the system water-chloroform. The results are represented graphically in Figure 1. Based on the concentrations of the complex in the organic phase, the extraction of the above-mentioned cations with **1b** is slightly more efficient than with the monomer **15-O<sub>5</sub>**. The most interesting observation is that the dimer **1b** displays higher selectivity than the monomer **15-O<sub>5</sub>** in favour of  $Na^+$ , with respect to the other alkali cations. Furthermore, the dimer **1c** extracts better the cations  $Li^+$ ,  $Na^+$  and to a lesser degree  $K^+$ , than does the monomer. This dimer also distinguishes more strongly between cations  $K^+$  and  $Rb^+$  than does the **18-O<sub>6</sub>** crown ether. Neither the dimer **1a** nor the monomer **12-O<sub>4</sub>** gave any significant extraction of alkali picrates in the same conditions.

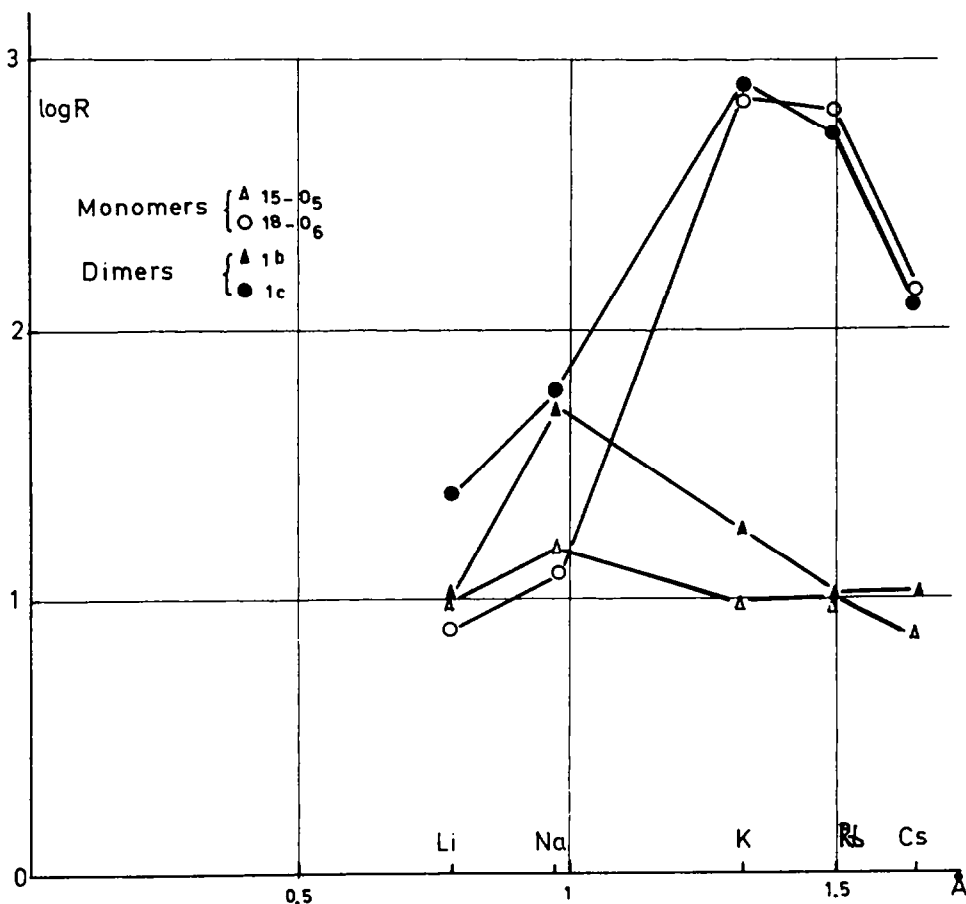


Figure 1. Graphical representation of the alkali picrate extraction abilities of the dimers 1b and 1c and of the corresponding monomers 15-O<sub>5</sub> and 18-O<sub>6</sub> as a function of ionic radius of the alkali cations;  $R = \frac{[LM^+P^-]_{org} \cdot v_{org}}{[L]_{org} \cdot [M^+]_{aq} \cdot v_{aq}}$ , where  $[LM^+P^-]_{org}$ ,  $[L]_{org}$  and  $[M^+]_{aq}$  are respectively the concentration of complex in the organic phase and the initial concentrations of ligand in the organic phase and cation in the aqueous phase;  $v_{org}$  and  $v_{aq}$  are the volumes of the organic and aqueous phases.

#### EXPERIMENTAL

NMR spectra were recorded on a Varian XL-200 spectrometer in CDCl<sub>3</sub> solutions unless stated otherwise. Multiplicity of <sup>13</sup>C NMR signals is indicated for one bond couplings as S, D, T, Q, M and s, d, t, q, m, for long-range couplings. Mass spectra were registered on Varian MAT 44S spectrometer.

#### General procedure for BDH of crown ethers :

A benzene (160ml) solution of the corresponding crown ether (164 mmol) and DTBP (8.2 mmol)-molar ratio 20/1 - is irradiated under argon by a 150W high pressure Hg-lamp for 48 hrs at room temperature. Benzene is removed in vacuo and the excess of the crown ether is removed by Kugelrohr distillation in high vacuum (10<sup>-3</sup> Torr). Further fractionation affords the dimers 1a,b,c as mixtures of meso and d,l.

**Dimer 12-O<sub>4</sub>-12-O<sub>4</sub> 1a :** Slowly crystallizing oil, B.p. 140-45°/10<sup>-3</sup> Torr; <sup>1</sup>H NMR 3.5-3.9(m)<sup>4</sup>; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ = 71.6-71.9, 72.0 (T); 80.5 and 80.8 (D); MS : DCI (isobutane) (M+1)<sup>+</sup> = 351; found : C, 54.31; H, 8.88; O, 36.23. C<sub>16</sub>H<sub>30</sub>O<sub>8</sub> requires : C, 54.84; H, 8.63; O, 36.53.

**Dimer 15-O<sub>5</sub>-15-O<sub>5</sub> 1b :** oil of B.p. 180-85°/10<sup>-3</sup> Torr; <sup>1</sup>H NMR = 3.41-3.81(m); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ = 70.4-79.2 (T); 79.9 and 80.0 (D); MS : EI M<sup>+</sup> = 438; DCI (H<sub>2</sub>O)

(M+1)<sup>+</sup>=439.

**Dimer 18-O<sub>6</sub>-18-O<sub>6</sub> lc** : Oil of B.p. : 210-15°/10<sup>-3</sup> Torr ; <sup>1</sup>H NMR = 3.42-3.84(m) ; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ = 71.3-72.0 (T), 80.2-80.3 (D) ; MS : DCI (isobutane) (M+1)<sup>+</sup>=527.

**General Procedure for BDHD of crown ethers : Procedure A** : Crown ether (0.1 mol), **2** (1.41g, 0.01 mol) and DTPO (1.17g, 0.005 mol) are placed in an ampoule which is degassed in three freeze-thaw cycles, sealed and heated to 60° for 8 hrs. Excess crown ether is removed as indicated above and the residue is recrystallized or chromatographed.

**Procedure B** : Crown ether (0.5mol), **2** (1.41g, 0.01 mol) and DTBP (0.73g, 0.005 mol) are irradiated in 160 ml benzene as indicated for **1a-c** including the work-up.

**Procedure C** leading to dismutation products : Same as for A using 0.73g DTBP and heating to 140° for 12 hrs.

**3a and 3b**, recryst. from ether gives one diastereomer each **3a** ; M.p. 191°. <sup>1</sup>H NMR δ=1.60(s,18H) ; 1.47(dd,2H) <sup>2</sup>J=14.0 Hz, <sup>3</sup>J=8.8 Hz ; 2.45(dd,2H) <sup>2</sup>J<2Hz ; 3.7-3.8(m,28H) ; 4.15(dd,2H) ; MS : DCI(isobutane) (M+1)<sup>+</sup>=633 ; 577, 521, 473, 417, 374, 318, 262, 177, 57, 41 ; Found : C, 56.82 ; H, 8.25 ; S, 10.27 ; O, 20.40. C<sub>30</sub>H<sub>52</sub>S<sub>2</sub>N<sub>2</sub>O<sub>8</sub> requires : C, 56.93 ; H, 8.28 ; S, 10.13 ; O, 20.22.

**3b** : M.p. ether, M.p. 182-83°. <sup>1</sup>H NMR δ=1.60(s,18H) ; 1.47(dd,2H) <sup>2</sup>J=14.2 Hz, <sup>3</sup>J=8.8 Hz ; 2.48(dd,2H) <sup>2</sup>J<2 Hz ; 3.75-3.9(m,36H), 4.13(dd,2H) ; MS : DCI (isobutane) (M+1)<sup>+</sup>=721 ; 665, 631, 501, 461, 418, 362, 336, 306, 195, 133, 57, 41 ; Found : C, 56.10 ; H, 8.29 ; S, 9.08 ; O, 22.96. C<sub>34</sub>H<sub>60</sub>S<sub>2</sub>N<sub>2</sub>O<sub>10</sub> requires : C, 56.64 ; H, 8.38 ; S, 8.89 ; O, 22.19.

<sup>13</sup>C NMR of **3a** and **3b** (in brackets), for numbering see Scheme 3.  
C(CH<sub>3</sub>)<sub>3</sub> : δ = 31.8 (31.5) Q sept ; -CH<sub>2</sub>-C<sup>-</sup> : 41.8(41.4) Tm ; CMe<sub>3</sub> : 50.9(50.6) Sm  
-C<sup>-</sup> : 54.5(54.1) Sm ; Ring carbons : C<sub>1</sub> : 69.5) Tm ; C<sub>2</sub> : 74.0(73.2) Tm ; C<sub>3</sub> : 76.5(76.3) Dm and at δ = 70.3, 70.4, 70.6, 70.8, 71.0(70.2), 70.3, 70.4, 70.6, 70.8) Tm ; CN : 116.6(116.4) Sd, <sup>2</sup>J=10 Hz.

**Dismuted products 4ab, 5ab, 6ab** are isolated by column chromatography as 1:1 mixtures of **a** and **b**. They represent viscous oils and no further separation was attempted at this moment. The components were characterized by the NMR spectra of the mixtures. **4a, 5a** and **6a** : <sup>1</sup>H NMR δ = t-Bu : 1.40, s ; -CH<sub>2</sub>- : 1.8-2.3, m ; S-CH-CN and ring protons : 3.6-3.7, m. <sup>13</sup>C NMR of **6a** (mixture of threo and erythro forms) S-CH-CN : δ = 25.7, 26.1 Dm ; C(CH<sub>3</sub>)<sub>3</sub> : 3.7 Q. sept. ; C-CH<sub>2</sub>-C : 35.9, 36.6 Tm ; CMe<sub>3</sub> : 44.8, 44.9 Sm ; ring CH<sub>2</sub> : 69.5-72.8 Tm ; ring CH : 76.5-78.3 Dm ; CN : 120.9, 121.7 Sm.

**4b (5b, 6b)** : <sup>1</sup>H NMR of the E isomer δ = t-Bu : 1.40, s ; ring protons : 3.6-3.7, m ; HC= 6.56 (6.66, 6.60), d, <sup>2</sup>J = 9 Hz. <sup>13</sup>C NMR for **6b, E** (6b, Z in brackets) δ = C(CH<sub>3</sub>)<sub>3</sub> : 30.07(31.0) Q.sept. ; CMe<sub>3</sub> : 47.8(48.7) Sm, ring CH<sub>2</sub> : 69.5-72.8 Tm ; ring CH : 76.5-78.3(75.2) Dm ; C(CN)SR : 107.8(109.6) Sm, <sup>2</sup>J<sub>1</sub> = 4Hz ; CN : 116.7ppm <sup>3</sup>J=13.5 Hz (117.8 ppm, <sup>2</sup>J ≈ 7 Hz) Sd ; HC= : 159.2 ppm, <sup>1</sup>J = 163.0 Hz(155.3 ppm) Dm.

**Acknowledgements** : We thank the "Ministère de la Programmation Scientifique" for a grant (79/84-13). Further we are indebted to IRSIA and to Rhône-Poulenc Industries for a grant to M.B. and S.M., respectively.

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