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Laser-induced dealkylation of calix[4]arene-crown-6 ethers

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Abstract

Selective dealkylation of dialkyl calix[4]arene monocrown-6 and calix[4]arene biscrown-6 was achieved using laser irradiation. The resulting phenolic compounds structures, studied by NMR (^1H and ^{13}C) and ESI-MS (Cs^+ spiking), probably originated from their partial photo-Claisen rearrangement.

Keywords: Calix[4]arene crown-6; Dealkylation; Cs^+ extraction; Laser

1. Introduction

The stability of calix[4]arene-crown-6 ether compounds under extreme degradation conditions is of crucial importance, mainly because of their use as extractants of $^{135}Cs^+$ and $^{137}Cs^+$ from the nitric acid slurries used in the reprocessing of spent nuclear fuel [1–6]. Crown-6 and 1,3-alternate calix[4]arene-crown-6 systems have been shown to be an apt choice to selectively complex these metal cations, as they have a crown net which perfectly matches the Cs^+ cation's size according to the rules of host–guest inclusion [7,8]. When subjected to radiolysis in nitric acid solution, the calix[4]arenes undergo several modifications, such as oxidation or nitration. Three particular calix[4]arene-crown-6 compounds have been intensively studied and can be considered reasonably resistant to the aforementioned radiolytic conditions: the two monocrown compounds, *i*PrMC-6 and *n*-octMC-6 and one biscrown compound, BC-6 (Fig. 1).

In our previous work, we have shown that even under extended radiolysis (simulated for 1 or 3 years via γ-radiolysis of ^{60}Co bomb, or from real-life samples), *i*PrMC-6 and BC-6 resist degradation, especially in the absence of HNO_3. For *n*-octMC-6, radiolysis leads to the same result (from 52 to 75% of recovery of calix[4]arene) [2].

During radiolysis of the MC-6 and BC-6 series, the compounds *i*PrMC-6 and *n*-octMC-6 undergo a certain amount of dealkylation, as opposed to crown destruction (in the case of the BC-6 compound, the loss of C_2H_4 or C_2H_4O units from the crown was observed via electrospray mass spectrometry).

One difficulty in working with calixarenes is their general poor solubility in organic solvents; this problem is often resolved by the introduction of the crown ether moiety (phenol ether). After radiolytic dealkylation and/or crown damage, this problem reoccurs, hindering the quantification of the process due to lessened solubility.

To further examine the stability of the calix[4]arene-crown, we would like to evaluate the degradation of its aromatic moiety (by, e.g., nitration) and the modification of its crown moiety. In particular, the use of softer degradation methods (such as ultrasound, microwave, or laser) could lead to the selective modification of the calix-crown.

2. Experimental

2.1. Materials

All calix[4]arene-crown compounds were purchased from Acros Chemicals (France) or were provided within the CEA network.

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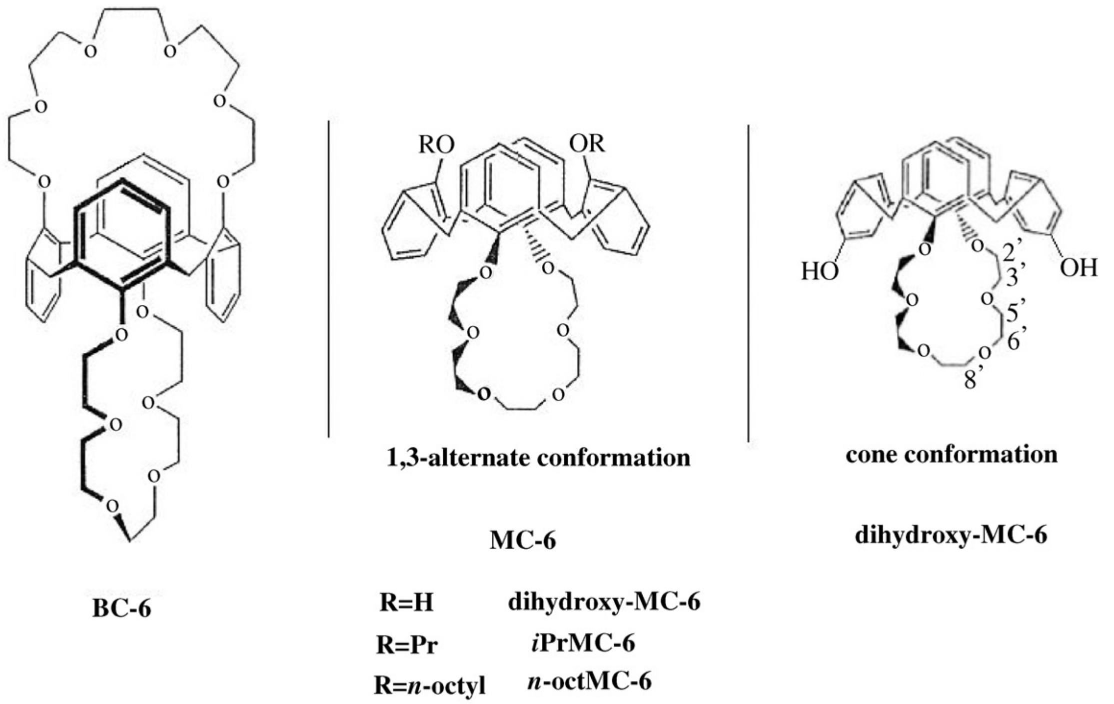


Full names of compounds above:
dihydroxyMC-6 : 25,27-dihydroxy-calix[4]arene-26,28-crown-6
***i*PrMC-6**: 25,27-diisopropoxy-calix[4]arene-26,28-crown-6
***n*-octMC-6**: 25,27-di-n-octyloxy-calix[4]arene-26,28-crown-6
BC-6: calix[4]arene-25,27,26,28-crown-6

Fig. 1. Structures of calix[4]arene compounds.

25,27-bis(2-Propyloxy)calix[4]arene-26,28-crown-6 (*i*PrMC-6) and 25,27-bis(1-octyloxy)calix[4]arene-26,28-crown-6 (*n*-octMC-6) were both identified as being in 1,3-alternate conformation (^{1}H and ^{13}C NMR spectra of benzylic protons and carbon signal as assumed in Refs. [4] and [10]).

25,27-Dihydroxycalix[4]arene-26,28-crown-6 (dihydroxyMC-6) in cone conformation was synthesized according to the slightly modified Casnati procedure [4] (CH_2Cl_2 solution, room temperature, addition of 10% excess of hydride then 30 min. of reflux under Ar; yield: 50% of crude diphenol, recrystallized yield: 28%).

The same product and starting calix[4]arene were separated from laser mixture by flash column chromatography (silica gel, hexanes or cyclohexane/ethyl acetate 4:1 eluent). The preliminary identification of laser mixtures was performed on commercial TLC pre-coated plates (silica gel, F254, aluminum sheets) and were visualized under UV light. The molecular modeling was performed on HyperChem MM+ 6.03 as described in our previous paper [13].

2.2. NMR spectroscopy

The ^{1}H and ^{13}C spectra were recorded on Bruker AC300 and on AC200 MHz apparatuses as $CDCl_3$ solutions. All detailed NMR spectra are available on request from the corresponding author. All deuterated solvents were purchased from Eurisotop or Aldrich Chemicals.

2.3. Laser photolysis

10^{-3} M chloroform solution of three calix[4]arene-crown-6 (100 mg each) were subjected separately to laser photolysis in the following manner:

The experimental setup consists in an excimer laser (Lambda Physik, EMG 203 MSC) operation at 308 nm (XeCl) and delivering about 200 mJ in a 25 ns pulse with a repetition rate adjustable from 1 to 200 Hz. For the photolysis experiments, repetition rate was set to 50 Hz. The laser beam is then directly sent into a quartz cell which contains the solution and the output power before and after the cell is measured by a wattmeter (Sciencetech) in order to control the elimination [11,12].

2.4. Electrospray-mass spectrometry (ESI-MS)

The ESI-MS experiments were recorded on triplequad Quattro II apparatus (Micromass, Manchester, UK) as described in Ref. [3] using CsCl solution to cationize the calix[4]arene-crown-6 derivatives.

3. Results and discussion

In this study, we described the behavior of three calix-[4]arene-crown compounds (*i*PrMC-6, *n*-octMC-6 and BC-6) when subjected to 308 nm laser photolysis as 10^{-3} M solu-

Table 1
Laser Induced dealkylation yields

CAL	Total recovery of organic material (%)	DihydroxyMC-6 yield[a] (%)	Starting material recovery[b] (%)	Polymeric residue recovery[c] (%)
BC-6	50	35	50–53	<15
*i*PrMC-6	50	20	55–57	15–20
octMC-6	60	10	70–77	15–20

[a] From TLC (quantitative), column chromatography and ESI-MS.

[b] As estimated from ESI-MS with Cs$^+$ and Na$^+$ spiking.

[c] Unidentified.

Table 2
The NMR (^{1}H and ^{13}C) of dihydroxyMC-6

^{1}H					^{13}C		
Position	δ (ppm)	Mult.	$J_{\mathrm{H–H}}$ (Hz)	Integration	δ (ppm)	Mult.	Position
OH	7.49[a]	s	–	2H	153.3	s	Ar, ipso
ArH, meta	7.07	d	7.6	4H	152.1	s	Ar, ipso
ArH, meta	6.83	d	7.6	4H	133.1	s	Ar, ortho
ArH, para	6.70	t	7.6	2H	128.2	s	Ar, ortho
ArH, para	6.68	t	7.6	2H	129.0	d	Ar, meta
ArCH$_2$Ar	4.43	d	14	4H	128.5	d	Ar, meta
Crown-6(H2′)	4.15	t	4.8	4H	125.3	d	Ar, para
Crown-6(H3′)	4.01	t	4.8	4H	118.9	d	Ar, para
Crown-6(H5′)	3.93	t	4.8	4H	76.4	t	Crown-6
Crown-6(H6′)	3.84	t	4.8	4H	71.6	t	Crown-6
Crown-6(H8′)	3.70[b]	s	–	4H	71.0	t	Crown-6
ArCH$_2$Ar	3.38	d	14	4H	69.9	t	Crown-6
	5.30				31.1	t	ArCH$_2$Ar

Solvent peak 5.30 and 1.18 ppm.

[a] D$_2$O exchange.

[b] Broad.

tion in chloroform. The total recovery of chloroform-soluble products was high (50–60%) (Table 1). The mixtures displayed a common pattern: the presence of starting material at variable levels (50–77%), the unidentified polymeric residue (probably polyphenols, 15–25%), and a product (diphenol calix[4]arene) present in all three photolytic mixtures, described as a diphenol mono-crown derivative (dihydroxyMC-6, 10–35%).

If for the two MC-6 calixarenes the origin of this diphenol is the dealkylation, then for the BC-6 it should come only from the destruction of one of the two crowns. Curiously enough, the diphenol yield in this case is higher than for the two MC-6 products, and the *n*-octMC-6 photolysis produces twice as much of the diphenol as does the *i*PrMC-6. However, the most resistant of the three to laser-induced photolysis seems to be the *n*-octMC-6 (up to 77% of starting material recovered). The only

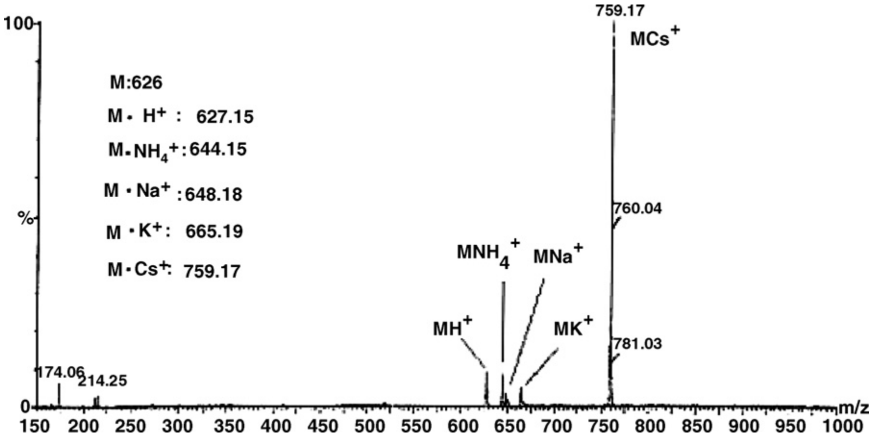


Fig. 2. ESI-MS spectrum of dihydroxyMC-6.

reasonable yield of the diphenol was then obtained from BC-6, in which case one of two crowns is destroyed. For the two others, the dealkylation is substantially more favored than is the destruction of the crown.

Next, we sought to confirm the identity and the conformation of this diphenol, which we synthesized according to slightly modified Casnati and Ungaro method [9]. After its separation from the BC-6 laser photolysis mixture, the diphenol was compared to the original synthetic sample under ESI-MS, after spiking of the solution with CsCl. The intense MCs^+ ion at *m*/*z* 758 was observed along with the MNa^+ ion at *m*/*z* 648 (Fig. 2). All reaction mixtures also showed the starting calixarene MCs^+ ions at *m*/*z* 848 (*i*PrMC-6), 983 (*n*-octMC-6), 961 (BC-6) and MNa^+ at *m*/*z* 851 (BC-6), 733 (*i*PrMC-6), 873 (*n*-octMC-6).

The NMR (^1H and ^{13}C) of this diphenol presents some interesting details (Table 2, Fig. 3). The NMR spectrum shows very well separated crown signals corresponding to C'_2–C'_8 protons. The benzylic protons signals showed the AB systems (at 3.38 and 4.43 ppm) indicating the cone conformation of this dephenol. It is interesting to notice that the starting calix[4]arene-crown-6 compounds were in 1,3-alternate conformation (e.g. *i*PrMC-6: all benzylic protons at 3.80 ppm). This observation was additionally confirmed by the ^{13}C signals for benzylic carbon at 31.1 ppm for dihydroxyMC-6 obtained, again the cone conformation of resulting conformer compound (instead of 37–38 ppm if the 1,3-alternate one) is adopted.

The stability of this diphenol could not be explained by the interphenolic or phenol-crown H-bonds in all adopted conformations (which was not observed in the molecular modeling experiments). The rotation of one phenol-bearing ring around the mobile benzylic system of starting 1,3-alternate compound lead to the stabilization of the molecule mostly in cone conformation. The calculated energies of three conformations are shown in Fig. 4.

However, the benzylic coupling for the diphenol (NMR in $CDCl_3$, $J = 14$ Hz) and chemical shift difference between two benzylic protons ($\Delta\delta = 1.06$ ppm) clearly indicate its presence in the cone conformation [10].

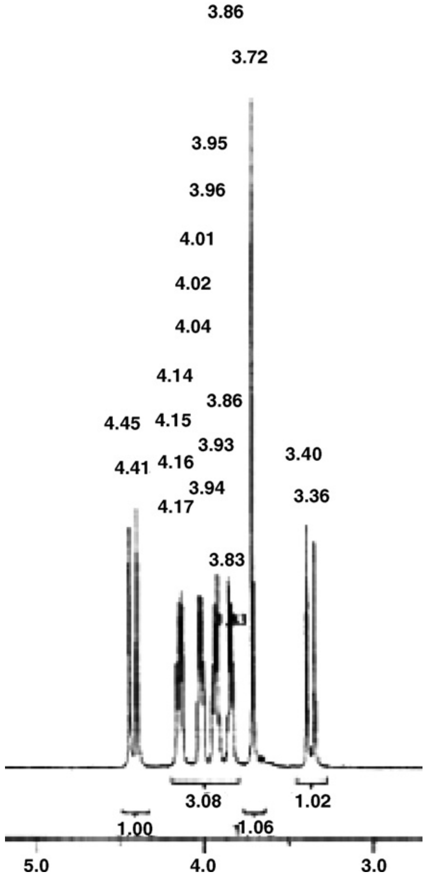
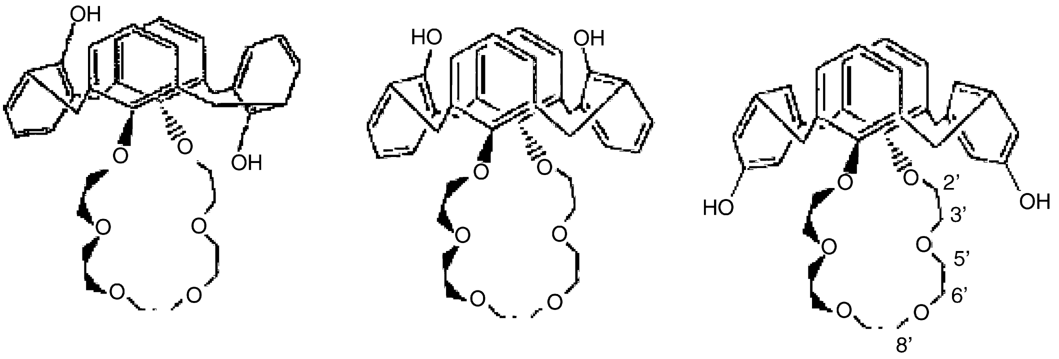


Fig. 3. Partial 300MHz ^1H NMR spectrum of dihydroxyMC-6.

The specific laser wavelength used (308 nm) was chosen both for adequate and efficient UV absorption of the calixarene crown compounds and powerful UV laser capabilities [11,12]. It seems reasonable to excite the molecule at this wavelength because of its 2,6-dialkylaryl chromophore character.

The two other techniques mentioned (microwave and ultrasound) did not lead to any dealkylation or crown removal under any of several combinations of experimental parameters (dura-



Partial cone
19.01 kcal/mol

1,3-alternate
17.83 kcal/mol

cone
26.79 kcal/mol

Fig. 4. Conformations of dihydroxy calix[4]arene-mono-crown-6.

tion, power, nature of solvent, presence of HNO_3-no nitration under microwave conditions) [14].

4. Conclusion

The use of laser photolysis to selectively degrade and/or modify calixarene-crown compounds was designed as a softer alternative to radiolysis in the search for specific degradation products.

From this perspective, the potential applications of lasers for specific crown removal from calixarene-crown-cyclodextrin supramolecular aggregates (such as have been recently synthesized [13]) are limited to the BC-6 case, where single-crown removal could be expected.

From this preliminary study, it seems clear that 308 nm-laser-induced photolysis enabled the selective removal of either alkyl or crown from the calix[4]arene in the presence of alkylated phenolic ether groups. It is possible that the UV laser treatment will become an alternative method to change the 1,3-alternate into the cone conformation for calix[4]arene-crown compounds. The use of lasers of other wavelengths was considered for eventual further experimentation. However as already mentioned microwave and ultrasound techniques seems to be too soft to remove either crown or alkyl moieties [14].

The thermal reaction on aryl ether compounds often leads to Claisen rearrangements. In a case of photochemical reactions, the photo-Claisen rearrangement could take place producing the ortho to para rearranged products (difficult in this case because of the crown-calixarene rigid structure) as well as to the phenols [15]. This rearrangement and its mechanisms were remarkably well abstracted by Galindo [16]. The phenols observed through the photo-Claisen rearrangements are the results of radical stepwise mechanisms [17] with the homolytic C–O bond cleavage.

The other phenolic species for the crown-calixarenes were not identified, probably because of the lack of appropriate standards and their easy polymerization.

However, it is probably useless to apply the lasers at lower wavelength because the reaction probably occurs via S_1 excited state [18]. The full crown-calixarene-cesium complexes could be subjected to the laser treatment. In this manner the Cs^+-complex behavior could be compared to that of the host alone.

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