Tetrahedron 67 (2011) 8092–8101

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Narrow rim CMPO/adamantylcalix[4]arenes for the extraction of lanthanides and actinides

Ivan Vatsouro [a], Alina Serebryannikova [a], Leyong Wang [b], Véronique Hubscher-Bruder [c,d], Elvira Shokova [a], Michael Bolte [e], Françoise Arnaud-Neu [c,d], Volker Böhmer [b], Vladimir Kovalev [a,*]

[a] Laboratory of Macrocyclic Receptors, Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russia
[b] Abteilung Lehramt Chemie, Fachbereich Chemie, Pharmazie und Geowissenschaften, Johannes Gutenberg Universität, 55099 Mainz, Germany
[c] Université de Strasbourg, IPHC, 25 rue Becquerel, 67087 Strasbourg, France
[d] CNRS, UMR 7178, 67037 Strasbourg, France
[e] Institut für Anorganische Chemie, Johann Wolfgang Goethe-Universität, 60439 Frankfurt/Main, Germany

ARTICLE INFO

Article history:
Received 11 April 2011
Received in revised form 4 August 2011
Accepted 22 August 2011
Available online 27 August 2011

Keywords:
Calixarenes
CMPO-ligands
Actinide/lanthanide extraction
Functionalization
Mixed functionalities

ABSTRACT

Six *p*-(1-adamantyl)calix[4]arenes **7**, **8** with four differently attached diphenyl-carbamoylmethyl phosphine oxide (CMPO) functions at the narrow rim were synthesized. This series was extended by adamantylcalix[4]arenes with two CMPO and two ester, acid or (diethylphosphono)acetylamino groups. Structures of new compounds were proved by NMR, mass-spectrometry and a single-crystal X-ray analysis for the intermediate di-phthalimide $\mathbf{10_3}$. The extraction studies towards selected lanthanides and thorium showed that the ligands **7** surpassed the corresponding *p*-H, *p*-*tert*-butyl and *p*-*tert*-octyl analogues **3**–**5** in lanthanide extraction while thorium was extracted with the same or lesser extent. For the lanthanide extraction $D_{Ln}(\mathbf{7_4}) > D_{Ln}(\mathbf{7_3}) \approx D_{Ln}(\mathbf{7_2})$, which follows the order established earlier for ligands **3**–**5**. Among the tetra-CMPO derivatives of type **8**, the ligand $\mathbf{8_{3/4}}$ was the best extractant for which the D_{Ln} and D_{Th} values were comparable with those for $\mathbf{7_4}$.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

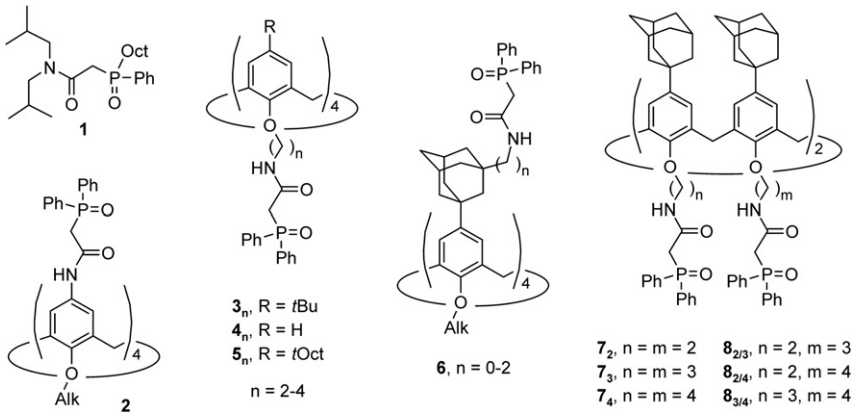
Nuclear waste treatment is currently an important task aimed at reducing the amount and activity of toxic nuclides to be stored. The removal of uranium and plutonium from irradiated nuclear fuel (industrial PUREX process)[1] results, unfortunately, in a significant volume of highly acidic solutions containing numerous long-lived radionuclides. Several industrial extraction processes have been developed for the reprocessing of these acidic solutions; the TRUEX process utilizing CMPO ((*N*,*N*-diisobutylcarbamoylmethyl)octylphenylphosphine oxide, **1**, Scheme 1) as an extractant is one of them.[2,3] Although the extraction level provided by CMPO-like ligands is high, more effective and much more An/Ln selective ligands are necessary to meet the current ecological requirements.

As the extracted complex contains three molecules of bidentate CMPO per cation,[4,5] a significant improvement of the extraction ability of ligands can be achieved by pre-organization of several CMPO-like groups on a common platform,[6] including calixarenes, which have been studied in a broad range of structural variations. Thus, four CMPO-like groups were grafted onto the wide or narrow rim of *cone* calix[4]arene scaffold to get ligands of types **2**–**5**, which are highly efficient for *f*-element extraction.[7–12] The first CMPO/calixarenes rigidified in the 1,3-*alternate* conformation have also been recently reported.[13]

In line with our research in adamantylcalix[4]arene chemistry we have created efficient actinide/lanthanide extractants of type **6** in which the adamantane units served as linkers between calixarene core and CMPO groups.[14,15] We have also established previously a high extraction ability of the *p*-(1-adamantyl)calixarenes with four CMPO-groups attached to the narrow rim identically (compounds **7**) or in an alternating fashion (compounds **8**) towards 'hot' ^{241}Am and ^{152}Eu.[15] Here we describe in detail the syntheses of **7** and **8**, and related compounds with mixed functionalities obtained both by selective alkylation of the narrow rim of adamantylcalix[4]arene and an amine protection/deprotection route. In order to evaluate the influence of the adamantane units at the wide rim and the CMPO attachment mode at the narrow rim of calix[4]arenes onto the complexation properties of the ligands, a series of extraction experiments with selected lanthanides and thorium were conducted under conditions similar to those used earlier for the study of compounds **3**–**5**.

* Corresponding author. Tel.: +7 495 939 1302; fax: +7 495 932 8846; e-mail address: kovalev@petrol.chem.msu.ru (V. Kovalev).

0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2011.08.059



Scheme 1. CMPO-ligands used for discussions (**1**–**6**) and studied (**7**–**8**).

2. Results and discussion

2.1. Synthesis

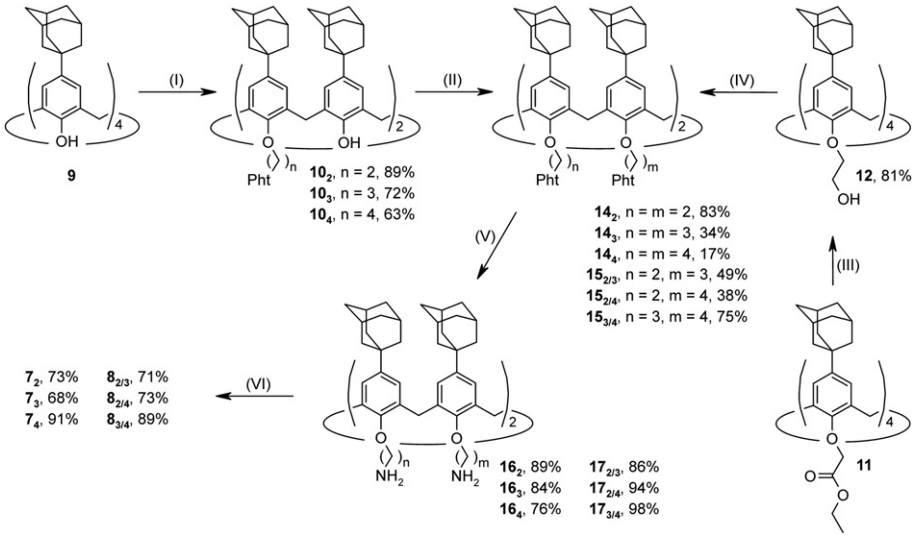
The narrow rim CMPO-derivatives of calixarenes appear to be easily available through the alkylation of the parent macrocycles with ω-bromoalkylphthalimides followed by hydrolysis and acylation with the phosphorous-containing active ester.[10] Nevertheless, the direct exhaustive alkylation of (1-adamantyl)calix[4]arene **9** with 3-bromopropyl- and 4-bromobutylphthalimides using NaH as the base did not lead to the desired tetra-alkylated calixarenes as the major products, while giving a complex mixture of compounds, that could be explained by the solubility issues. (The use of 2-bromoethyl phthalimide under these conditions was proved to be unsuccessful due to rapid HBr elimination from the reagent.[10]) Thus, other methods were required for the synthesis of the target calixarene derivatives.

The two-step alkylation of calixarenes can decrease the number of possible side-products compared with the exhaustive reaction and also expand the range of tetra-alkyl derivatives, which can be obtained when two different reagents are used. Adamantylcalix[4]arenes **10** were obtained from calixarene **9** in good yield by the selective alkylation with 3-bromopropyl- and 4-bromobutylphthalimides using K_2CO_3 as the base or by the selective Mitsunobu reaction with 2-hydroxyethylphthalimide[16] in the case of $\mathbf{10_2}$ (Scheme 2).

Upon re-crystallization from chloroform/methanol, colourless needles of $\mathbf{10_3}$ suitable for single-crystal X-ray analysis were obtained. In the crystalline state $\mathbf{10_3}$ possesses a *pinched cone* conformation stabilized with hydrogen bonds between OH groups and ether oxygen atoms (Fig. 1), and forms infinite chains due to the inclusion of one phthalimide group into the cavity of the neighbouring molecule (Fig. 2). The crystal data for $\mathbf{10_3}$ are collected in Table 1.

The further NaH-promoted alkylation of **10** gave the desired *cone* tetra-phthalimides $\mathbf{14_3}$, $\mathbf{14_4}$ and **15** in moderate to good yield. In the cases when the same alkylating reagent was used in both steps, the tri-phthalimides $\mathbf{13_3}$ and $\mathbf{13_4}$ were also obtained in 35 and 9% yield, respectively.

As the Mitsunobu condensation of (thia)calix[4]arenes with 2-hydroxyethylphthalimide is strongly selective, no tetra-alkylated products can be obtained by this method even when a large excess of reagents is used.[16,17] Assuming the mentioned difficulties with the $BrCH_2CH_2Pht$/NaH/DMF alkylation also in the case of $\mathbf{10_2}$, the synthesis of tetraphthalimide $\mathbf{14_2}$ required a completely different approach. In early examples, the aminoethyl functionalities have been introduced to the narrow rim of *p-tert*-butylcalix[4]arene by the tetraester reduction, tosylation of the tetrol, followed by reaction with NaN_3 and reduction.[10,18] The one step shorter and more efficient route was used for the modification of adamantylcalix[4]arene: the tetraester **11**[19] was reduced, and the resultant tetrol **12**



Scheme 2. Synthesis of tetra-CMPO derivatives **7** and **8**. (I) for n=2: $HO(CH_2)_2Pht$, Ph_3P, DIAD, THF; for n=3, 4: $Br(CH_2)_nPht$, K_2CO_3, CH_3CN; (II) for m=3, 4: $Br(CH_2)_mPht$, NaH, DMF; (III) $LiAlH_4$, THF; (IV) for n=m=2: HPht, Ph_3P, DEAD, THF; (V) $N_2H_4 \cdot H_2O$, EtOH/THF; (VI) *p*-nitrophenyl (diphenylphosphoryl)acetate, Et_3N, $CHCl_3$ or toluene.

Download English Version:

https://daneshyari.com/en/article/5220488

Download Persian Version:

https://daneshyari.com/article/5220488

Daneshyari.com