

## 摘要

Calixarenes 是酚和甲醛在鹼性催化的環境下，進行聚合反應所產生之環狀聚合物，其分子內具有中空的構型，因此可以藉由此特性，嵌合一些小型的有機分子或金屬離子，進而形成“主-客化合物”。理論上可以利用這種特性推廣應用於離子分離，微量檢驗以及酵素模擬的研究上。而本論文主要的目的是在合成出一系列未曾報導過之 1,2-雙烷基醚化之 calix[4]arenes。

*p*-*tert*-Butylphenol 和 甲醛在鹼環境的催化下，會進行聚合反應而形成黃綠色之聚合前驅物，將此聚合前驅物置於二苯醚 (diphenyl ether) 中迴流，可以轉換成 *p*-*tert*-butylcalix[4]arene (**1**)；然後利用三氯化鋁 (AlCl<sub>3</sub>) 作為催化劑，對環狀聚合物上的對位三級丁基，進行反向的 Friedel-Crafts 反應移除，即可得到對位無取代之 calix[4]arene (**6**)。

由於本實驗室在過去的研究中發現，calix[4]arene 和過量的鹵化烷類及 NaOCH<sub>3</sub> 在 CH<sub>3</sub>CN 中迴流，可一步合成出單烷基醚化之 calix[4]arenes；因此本論文採用了碘化乙烷 (iodoethane)，碘化正丙烷 (1-iodopropane)，碘化正丁烷 (1-iodobutane)，溴化甲苯 (benzyl

bromide) 和溴化丙烯 (allyl bromide) 等五種鹵化烷類，來製備此一系列單烷基醚化的 calix[4]arenes **29-33**。

這些單烷基醚化之 calix[4]arenes 可分別與 acetyl chloride 或 benzoyl chloride 進行酯化反應，而得到 1-烷基醚化-2,3-雙乙醯酯化之衍生物 **35-39** 及 1-單烷基醚化-3-單苯甲酸酯化之化合物 **51-55**。接著利用 NaH 及鹵烷類在 CH<sub>3</sub>CN 中，可分別對 1-單烷基醚化-2,3-雙乙醯酯化之 calix[4]arenes 及 1-單烷基醚化-3-單苯甲酸酯化之化合物進行第二醚化反應，本論文僅分離純化出 1,2-雙苯甲基醚化-3,4-雙乙醯酯化之 calix[4]arene **49** 及 1,2-雙烷基醚化-3-單苯甲酸酯化之 calix[4]arenes **56、57**。

針對化合物 **49** 的乙醯酯基和化合物 **56、57** 的苯甲酸酯基進行鹼性的完全水解，便可合成出 1,2-雙烷基醚化之 calix[4]arenes。這些在合成過程中之產物皆利用 <sup>1</sup>H-NMR、<sup>13</sup>C-NMR、COSY、NOESY、FAB-MS 的光譜分析來鑑定，在本論文中對合成和鑑定的過程均會做詳細的敘述與討論。

## Abstract

Calixarenes, which are cyclic oligomers of *p*-substituted phenols and formaldehyde, are able to include small organic molecules or metal ions within the molecular cavities to form “ host-guest ” complexes. These phenomena have been proposed in the applications of micro- analysis, ion separation, and enzyme-mimic studies. The main purpose of this thesis is to study the synthesis of calix[4]arene 1,2-dialkyl ethers, which was not available in the literature.

In the basic conditions, *p*-*tert*-butylphenol were polymerized with formaldehyde to form a yellowish precursor. Refluxing of this precursor in diphenyl ether yielded the *p*-*tert*-butylcalix[4]arene (**1**). The *p*-*tert*-butyl groups were removed by AlCl<sub>3</sub>-catalyzed reverse Friedel-Crafts reaction to give a parent calix[4]arene (**6**).

In our earlier studies on the calix[4]arene ethers, we have noticed that the monoalkylated calix[4]arenes can be prepared by refluxing calix[4]arene with alkyl halides in CH<sub>3</sub>CN with the presence of sodium methoxide as the reacting base. Five different alkyl halides, iodoethane, 1-iodopropane, 1-iodobutane, allyl bromide, and benzyl bromide, were applied in this synthetic procedure to achieve the preparation of monoalkylated calix[4]arenes **29-33**

Esterification of those monoalkylated calix[4]arenes with excess amount of acetyl chloride or benzoyl chloride yielded the corresponding diacetate products, **35-39** and monobenzoate products, **51-55**. Compounds **35-39** and **51-55** were treated with NaH and alkyl halides in order to introduce a second ether linkage. In this thesis we were only able to isolate 25,26-diacetoxy-27,28-dialkoxycalix[4]arenes (**49**) and 25,26-dialkoxy-27-benzoxy-28-hydroxy calix[4]arenes (**56**)-(57).

The removed of acetate and benzoate moieties in basic conditions yielded the corresponding vicinal 1,2-dialkoxy calix[4]arenes.

All the new products which were produced in this thesis were characterized by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , COSY, and FAB-MS. The synthetic procedure for vicinal 1,2-dialkoxycalix[4]arenes were also discussed in this thesis.