

## 摘 要

Calixarenes 是酚和甲醛於鹼性溶液中，進行催化聚合反應而得到的環狀聚合產物，因其分子內具有杯形中空的結構型狀，所以可以藉由此結構特性與一些小型的有機分子或金屬離子產生嵌合的現象，進而形成“主-客化合物”，這種嵌合特性可應用於微量檢驗、離子分離和酵素模擬的研究上。本論文主要的目的為合成出一系列 1,2-雙烷基醚化之 calix[4]arenes。

在鹼性條件的催化下，*p*-*tert*-butylphenol 與甲醛溶液，可聚合得到黃綠色的固態前驅物，將此聚合前驅物置於二苯醚(diphenyl ether)中進行迴流，可被轉換成 *p*-*tert*-butylcalix[4]arene (1)；如再以三氯化鋁 (AlCl<sub>3</sub>) 作為催化劑，進行反向的 Friedel-Crafts 反應來移除環狀聚合物上的對位三級丁基，便可得到對位無取代之 calix[4]arene (6)。

過去本實驗室的研究發現，calix[4]arene 與過量的鹵化烷類及 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；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，來製備一系列之單烷基醚化的 calix[4]arenes (29-33)。

若將所得到單烷基醚化之 calix[4]arenes (29-33) 與 benzoyl chloride 進行酯化反應時，可分別得到 1-單烷基醚化-3-單苯甲酸酯化之化合物(34-38) 及 1-單烷基醚化-2,3-雙苯甲酸酯化之化合物(39-43)；利用 NaH 及鹵烷類可對 1-單烷基醚化-3-單苯甲酸酯化之化合物(34-38)在 CH<sub>3</sub>CN 中，進行第二次烷基醚化反應，而得到 1,2-雙烷基醚化-3-單苯甲酸酯化之 calix[4]arenes (44、45)。

而本論文最終的目的即是對化合物 44、45 進行苯甲酸酯基之水解，以合成出 1,2-雙烷基醚化之 calix[4]arenes 46、47。這些合成的研究過程中之產物皆利用 <sup>1</sup>H-NMR、<sup>13</sup>C-NMR、COSY、FAB-MS 的分析來鑑定，在本論文中對合成和鑑定的過程均會做敘述與討論。



## 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.

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 AlCl<sub>3</sub> catalyzed reverse Friedel-Crafts reaction were then applied to remove the *p*-*tert*-butyl groups and gave parent calix[4]arene (**6**).

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

applied in this synthetic procedure.

Esterification of those monoalkylated calix[4]arenes **29-33** with an excess of benzoyl chloride in pyridine produced the corresponding 25-alkoxy-27-benzoyloxy-26,28-dihydroxycalix[4]arenes **34-38** and 25,26-dibenzoyloxy-27-alkoxy-28-hydroxycalix[4]arenes **39-43**. Products **34-38** were treated with NaH and alkyl halides in CH<sub>3</sub>CN to introduce the second alkyl ether linkage and yielded 25,26-dialkoxy-27-benzoyloxy-28-hydroxycalix[4]arenes **44**、**45**. The removal of benzoate moieties in basic conditions would yield the corresponding final products, 1,2-dialkoxycalix[4]arenes **46**、**47**.

All the new products which were produced in this thesis were characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, COSY, and FAB-MS. The synthetic procedure for 1,2-dialkoxycalix[4]arenes were also discussed in this thesis.