

摘 要

Calixarenes，為一種酚和甲醛的環狀聚合物，因為其具有分子內中空，故可以嵌合一些小型的有機分子或金屬離子，而形成“主-客化合物”，其特性可推廣應用於微量檢驗，離子分離及酵素模擬的研究；而本論文主要的目的是在研究在不同溶劑中，1,3-雙乙基醚化之 calix[4]diquinone 的兩種組態異構物相互轉換的速率。

p-*tert*-Butylphenol 和甲醛在鹼催化下可聚合成黃綠色之聚合前驅物 **26**，此一聚合前驅物於二苯醚 (diphenyl ether) 中迴流可被轉換成 *p*-*tert*-butylcalix[4]arene (**1**)；而此環狀聚合物上的對位三級丁基可再利用三氯化鋁 (AlCl₃) 作為催化劑，以反向的 Friedel-Crafts 反應移除，而得到對位無取代之 calix[4]arene (**6**)。

依據文獻報導，calix[4]arene 和鹵化烷類及 K₂CO₃ 在 CH₃CN 中迴流，可得到高產率的 1,3-雙烷基醚化之 calix[4]arenes；而本論文則採用了碘化乙烷 (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，來製備出相對應的 25,27-dialkoxy-26,28-dihydroxycalix[4]arenes (**27-31**)。當利用 ClO₂ 對雙乙基醚化之 calix[4]arene **27** 進行氧化時，反應後可分離得到，在室溫下能相互轉換之兩個組態異構物 *anti*-25,27-diethoxy-26,28-calix[4]diqui-

none (**32**) 和 *syn*-25,27-diethoxy-26,28-calix[4]diquinone (**33**)。

進一步的研究發現在不同溶劑中，*anti*-**32** 和 *syn*-**33** 組態的相互轉換速率也有所不同，因此本論文將探討 calix[4]diquinones **32** 及 **33** 在不同溶劑中 (CDCl₃, CD₃CN, acetone-d₆, benzene-d₆ 及 DMSO-d₆) 的動力學行為，並利用動力學一級反應的公式來計算出在不同溶劑中的轉換速率。



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 kinetic conversion rate between two conformational isomers of 1,3-diethoxycalix[4]diquinones.

In the presence of a base, *p*-*tert*-butylphenol and formaldehyde was polymerized, to form an yellowish precursor **26**. Refluxing of this precursor in diphenyl ether yielded the *p*-*tert*-butylcalix[4]arene (**1**). The *p*-*tert*-butyl groups were then removed with AlCl₃ by reverse Friedel-Crafts reaction to give the parent calix[4]arene (**6**).

Literature reported that calix[4]arene was dialkylated by refluxing with alkyl halides and K₂CO₃ in CH₃CN, and five different alkyl halides (iodoethane, 1-iodopropane, 1-iodobutane, benzyl bromide, and allyl bromide) were selected to give the corresponding *syn*-1,3-dialkoxy-calix[4]arenes **27-31**. The chlorine dioxide oxidation of 1,3-diethoxy-

calix[4]arene yielded two interconvertible conformational isomers of 1,3-diethoxycalix[4]diquinones (*anti*-**32** and *syn*-**33**).

It was observed that the interconversion rate between *anti*-**32** and *syn*-**33** was varied in different solvent system. Five solvent systems (CDCl₃, CD₃CN, acetone-d₆, benzene-d₆ and DMSO-d₆) was studied in this thesis, and the conversion rate constants of the *anti-syn* interconversion were measured.

