

行政院國家科學委員會專題研究計畫進度報告
電子效應與主客化學(1/2)
Electronic Effects and Host-Guest Chemistry (1/2).

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一、中文摘要

本計畫研究的主題為電子效應與主客化學。我們承續過去對2,5-雙取代金剛烷衍生物的研究，推展至2,4-雙取代金剛烷衍生物的合成，針對含羰基的化合物如2,4-雙羰基、4-羰基-2-亞甲烯基、以及4-羰基-2-硫酮基金剛烷衍生物(6-8)進行還原反應。針對含亞甲烯的化合物如7, 10進行Carbene addition反應、MCPBA氧化反應。對含fulvene的化合物如12, 13進行Diels-Alder addition反應、1,3-偶極環化加成反應，目前已有不錯的進展，已經投稿一篇於八月份的ACS Meeting，並已經被接受。

在主客化學上：合成上緣與下緣分別有不同取代的 Calixarenes：例如含偶氮及含硫取代的 Calixarenes 的合成。在上緣取代的 Calixarenes 之合成上，我們已利用丙烯基的重排及其反應多樣性，與 Nitroxides 行 1,3-偶極環化加成反應，製備了一系列上緣含 isoxazolinomethyl 取代基的 Calixarenes。除了已成功合成單 isoxazolinomethyl 取代的 Calixarene 之外，也合成了 5,11-, 5,17-雙取代的 Calixarenes，並利用氫核磁共振光譜技術探討此系列宿主對於四級銨鹽錯合的效用。已經發表一篇著作於周大紓教授

紀念專輯 (*J. Chinese Chem. Soc.* **2000**, *47*, 173-182).

未來對於上述1,3-偶極環化加成反應所獲得的不同取代之Calixarenes將進行各種開環反應：包括Raney Nickel 還原反應，TiCl₃ 偶合反應等嘗試。此外也將研究它們在金屬錯合或環境保護應用上的可能性。這些研究可以利用NMR, UV/VIS, Fluorescence等各種光譜法來分析。

關鍵詞：2,4-雙取代金剛烷衍生物、1,3-偶極環化加成反應、Isoxazolinomethyl-

calix[4]arenes

Abstract

This project is focused on two areas: The electronic effects and Host-Guest chemistry. We shall extend our work to the syntheses of 2,4-disubstituted Adamantanes and their application in face selectivity study. For example, Reduction reactions will be carried out on the carbonyl-containing compounds **6-8**. Carbene addition and MCPBA oxidation reactions will be applied to the methylene-containing compounds **7** and **10**. To fulvene-containing compounds we shall study their face selectivity in Diels-Alder reaction and 1,3-dipolar cycloaddition reactions.

Good progress is obtained in this area and we have submitted an abstract which will be presented in the Fall ACS meeting to be held in August in Washington DC.

In the Host-Guest chemistry: We have also extended our syntheses of upper-rim and lower-rim modified calix [4]arenes. For example, sulfur- and azo- containing calixarenes. In the upper-rim modification of calix[4]arenes, we used the Claisen rearrangement of allyl-group and its 1,3-dipolar cycloaddition reaction with nitrileoxides to furnish a series of isoxazolinomethyl containing calixarenes. Preliminary test of these hosts in the complexation of quaternary ammonium salts was studied using ^1H nmr spectroscopy. A paper has been published in the memorial issue of Prof. Ta-Shue Chou in *J. Chinese Chem. Soc.* **2000**, *47*, 173-182.

We shall also study the ring-opening reactions of those mono-, 5,11- and 5,17-diisoxazolomethylcalix[4]arenes obtained above, this includes Raney nickel reduction and TiCl_3 coupling reactions. Besides, we shall also explore the application of these upper- and lower rim modified calix[4]arenes in metal ion complexation and environmental protection. These types of research can be studied by nmr, uv/vis and fluorescence spectroscopy methods.

Key words: 2,4-disubstituted adamantanes, 1,3-dipolar addition, isoxazolinomethyl-calix[4]arenes.

二、緣由與目的

本研究是主持人持續進行的一個領域，而電子效應的探討在國內外也仍是個

非常熱門的主題，因為其進行機制仍有許多不清楚之處待釐清。

三、結果與討論

經由本研究我們獲得面向反應的過渡態能量差異與電荷分布差異，使得吾人對電子效應的機制更加清楚了解，特別是在沒有立體障礙差異的金剛酮系列，相對於靜電場效應來說過渡態超共軛理論扮演非常重要角色。詳見本人回顧性文章：*Chem. Review* **1999**, *99*, 1387-1413。

四、計劃成果自評

本計劃成果豐碩兩年來已發表論文五篇，分別是：(1) *J. Org. Chem.* **1999**, *64*, 1099-1107, (2) *J. Org. Chem.* **1999**, *64*, 2673-2679, (3) *J. Org. Chem.* **1999**, *64*, 6710-6716, (4) *Chem. Review* **1999**, *99*, 1387-1413, (5) *J. Chinese Chem. Soc.* **2000**, *47*, 173-182。

2. Purposes and Objectives

The study of electronic effects in various sterically unbiased trigonal carbon centers continues to attract considerable theoretical and experimental attention. Among the many models, transition-state hyperconjugation and electrostatic field interaction are the two most popular explanations for the face selectivity results to be found in the literature.

3. Results and Discussion

The effects of *p*-substitution of benzonitrile oxides (**5-Y**) on the face selectivity of 1,3-dipolar cycloaddition have been studied. 5-Substituted adamantan-2-ones and their derivatives have proven to be useful probes in research aimed at understanding the electronic factors in face selection. The studies of a variety of reactions indicate that the reagent prefers to attack the face antiperiplanar to the more electron-rich vicinal bonds, and the results can be reconciled with Cieplak's transition-state hyperconjugation model.

4. Self-Evaluation

Most of our work is fulfilled as originally proposed, and the results from two year's project have been sum up to **five** original publications: (1) *J. Org. Chem.* **1999**, *64*, 1099-1107 , (2) *J. Org. Chem.* **1999**, *64*, 2673-2679 , (3) *J. Org. Chem.* **1999**, *64*, 6710-6716 , (4) *Chem. Review* **1999**, *99*, 1387-1413 , (5) *J. Chinese Chem. Soc.* **2000**, *47*, 173-182.