

行政院國家科學委員會專題研究計劃結案報告

以雷射技術研究大氣化學之重要分子(II)-

雜環硫化物與碳六十的環加成及光解(3/3)

Using Laser Techniques in the Study of Important Molecules in Atmosphere (II)-

The Cycloaddition of Sulfur Containing Heterocycles with C-60 and Their Photolysis (3/3).

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一、中文摘要

本計劃為「以雷射技術研究大氣化學之重要分子 II」整合型研究計劃之子計劃，研究雜環硫化物與碳六十的環加成及光解(3/3)。

過去多年本實驗室從事許多含硫雜環化合物 Sultines 的合成，這些化合物是很好的雙烯基或雙自由基的前驅物。這些含硫有機化合物能同時被光解或熱解，這部分計畫已經和清大陳益佳及本所王念夏二位教授合作多年。目前我們除了已經建立雷射瞬態吸收光譜儀，也對幾個 Sultines 化合物進行雷射瞬態吸收光譜及其相關的動力學的量測，這部分工作已有不錯的結果，正在著手整理文稿之中。

當上述的 sultines 與 C₆₀ 進行高溫迴流，很容易脫去 SO₂ 產生活性極高的雜環 o-quinodimethanes，反應得到立體專一性的 1:1 Diels-Alder 加成產物，產率約 53~84%。變溫的碳核磁共振光譜亦支持上述的碳六十加成產物之構造，同時提供光譜與對稱性之關聯性的重要佐證。過去這一年我們合成了一系列 2,5-雙芳基吡咯雙自由基前驅物以及進行其光解與熱解實驗。我們首次獲得參態雙自由基的電子自旋共振光譜，與耶魯的 Berson 教授在 1997 年所發表的三篇 JACS 系列文章相符，然而也有不同於他們結果的重大新發現。

關鍵詞：雜環鄰萘二烯、2,5-雙芳基吡咯、

瞬態吸收光譜、電子自旋共振光譜、。

Abstract

This project is a joint effort in the application of laser techniques in the study of important molecules in atmosphere – The cycloaddition of sulfur containing heterocycles with C-60 and their photolysis (3/3).

In the past few years, we have focused on the synthesis of novel heterocyclic-fused sultines, precursors for o-quinodimethanes, and their application in Diels-Alder reactions. In collaboration with professors Chen, I.-C. and Wang, N.-S., we have studied their transient absorption spectra by laser flash photolysis of these sultines. Currently, we are studying the related kinetics of these reactive intermediates and their trapping with olefins. Meaningful results are obtained for these studies and several manuscripts are in preparation.

When heated in the presence of [60]fullerene, the sultines all underwent extrusion of SO₂ and the resulting heterocyclic-o-quinodimethanes were intercepted as the 1:1 adducts in 53% to 84% yields. Various temperature ¹³C-NMR spectroscopy also provides important information about the structure of cycloadducts and reveals interesting spectra and symmetry relationship. In the past one year, we have synthesized a series of 2,5-disubstituted pyrroles

and studied their photolysis and thermolysis reactions. ESR spectra of the triplet biradicals reported by Berson, J. A. (Yale University) were confirmed in our work, however, astonishing difference was also observed.

Keywords: *o*-quinodimethanes, 2,5-diarylpyrroles, transient absorption spectroscopy, Electron Spin Resonance Spectroscopy.

二、緣由與目的

雖然鄰萘二烯 **1** 已經廣泛被使用於製備碳六十的衍生物，但是雜環鄰萘二烯之重要性，直到最近才獲得相當的重視。目前已有許多產生此類高活性鄰萘二烯的方法，其中以從雜環駢 3-sulfolenes 脫去 SO₂ 的方法最常見。Quinoxalines 類化合物是天然物中存在的芳香雜環，他們通常具有生物活性及醫藥性質，因此找出一種容易合成且高產率生成雜環 quinoxalino-*o*-quinodimethanes 的方法，便成為研究上重要的課題。

Although *o*-quinodimethane **1** has been frequently been used for the derivatization of [60]fullerene, their heterocyclic analogues have been recognized only recently. Various methods for generating these highly reactive diene have been developed. Among them cheletropic elimination of SO₂ from hetero-aromatic-fused 3-sulfolenes has drawn the most attention. Quinoxalines are important naturally occurring heterocycles and are usually found to have biological and pharmaceutical activity. Finding an easy, high yield method for generating quinoxalino-*o*-quinodimethanes is thus of particular interest.

三、結果與討論

在這三年的研究計畫中，我們合成了許多新的 Sultines 化合物，這些 Sultines 化合物大多經由相關的雜環鄰二溴甲烷與 Rongalite (Sodium formaldehyde sulfoxylate) 試劑反應而得，產率一般大致在 55-76% 之間。在另一個子計畫中，我們也進行了 2,5-雙取代 吩 sultines 的合成，其反應與前述

quinoxaline 衍生物類似，經由相關的雜環鄰二溴甲烷與商業上可購得的 Rongalite (sodium formaldehyde sulfoxylate) 試劑反應而得，產率在 17-60% 之間。

若將 quinoxalinosultines 與一些典型的缺電性的親雙烯物反應，可以得到高產率的 1:1 或 1:2 加成的 Diels-Alder 產物。大部分時候這些反應也會有少量相關 sulfolenes 產物生成，但是與 sultines 類的高反應性所不同的是，這些 sulfolenes 並不會與親雙烯物反應，即使是高溫封管的溫度提高至 210 °C。

將碳六十與微過量的 quinoxalino-sultines 在鄰二氯苯中加熱迴流，不同的 sultines 其加熱時間不同，可以分別獲得碳六十的 1:1 加成產物，產率大約在 53-84% 之間。(詳細結果請參考著作: *J. Org. Chem.* 2000, 65, 3395.)

若將 2,5-雙取代 吩 sultines 與一些典型的缺電性的親雙烯物反應，sultines 5a-d 會脫去 SO₂ 的小分子，進而生成 non-Kekulé 的雙自由基分子 7a-d，然後與親雙烯物生成 1:1 的加成產物 8-12，產率大致在 50-85% 之間。Sultines 及 sulfolenes 與不同濃度的親雙烯物進行高溫裂解實驗，發現反應可能經由兩種途徑：其一為起始物與雙自由基中間物先達成平衡，另一則為 Diels-Alder 與 Retro-Diels-Alder 的反應機制；不過仍需更多實驗來驗證究竟何者正確。Sultine 5b 與正丁基鋰試劑反應發生親和性開環反應，經由水的處理之後得。另外，Sultine 5a 與甲醇、含氘取代甲醇 (methanol-*d*₄)、2-硫醇基乙醇等試劑一起在苯溶液中封管加熱，可以獲得約 1:1 的捕捉產物 19-21 與重排產物 sulfolene 6a。產物 19-21 的獲得，可以藉由加熱之後產生雙自由基或是離子中間物來解釋。(詳細結果請參考著作: *J. Org. Chem.* 2002, 67, 9267-9275.)

Previously unknown sultines were synthesized from the reaction of Rongalite with the known bis-(bromomethyl)- quinoxalines in 55-76% yield. The Diels-Alder reactions of

these sultines with typical dienophiles lead to high yields of 1:1 and 1:2 adducts in good to excellent yields. Small amount of sulfolenes were also formed, however, they did not react with any of these dienophiles even at 210 °C in contrast with the high reactivity of corresponding sultines.

When C₆₀ was refluxed in *o*-dichlorobenzene for a variable period of time with a slight excess of the quinoxalino-fused sultines, the 1:1 cycloadduct was obtained in 53-84% yield. (For details about this work, please refer to *J. Org. Chem.* **2000**, 65, 3395).

One of the subproject was involved in the syntheses of 2,5-disubstituted-thieno-sultines(5,7-disubstituted-1,4-dihydro-1*H*-3λ⁴-thieno-[3,4-*d*][2,3]oxathiin-3-oxides) **5a-d**, are prepared from the corresponding dichlorides **4a-d** with the commercially available Rongalite (sodium formaldehyde sulfoxylate) in 17~60% yields. When heated in the presence of electron-poor dienophiles, sultines **5a-d** underwent elimination of SO₂, and the resulting non-Kekulé biradicals **7a-d** were intercepted as the 1:1 adducts (**8-12**) in good to excellent yields. The pyrolysis of sultines and sulfolenes with different concentration of dienophiles revealed that either a pre-equilibrium between starting reagents and biradical species or a Diels-Alder and retro-Diels-Alder reaction mechanisms may be involved, however, more work is necessary to establish the proposed mechanisms. Reaction of sultine **5b** with *n*BuLi was found to undergo a nucleophilic ring-opening reaction to give sulfinyl alcohol **17** after H₂O work up. When sultine **5a** was heated in benzene in a sealed tube in the presence of methanol, methanol-*d*₄, or 2-mercaptoethanol, the respective 1:1 trapping adducts **19-21** as well as the rearranged sulfolene **6a** were isolated in similar amounts. The isolation of adducts **19-21** may be explained by the involvement of either biradical or ionic intermediates during the pyrolysis. (For details

about this work, please refer to *J. Org. Chem.* **2002**, 67, 9267-75).

四、計劃成果自評

本計劃大部份依原定計劃如期完成，已經發表論文三篇：(1) *J. Org. Chem.* **2000**, 65, 3395;(2) *J. Chinese. Chem. Soc.* **2002**, 49, 77;(3) *J. Org. Chem.* **2002**, 67, 9267-75。另外有一篇送審 *J. Am. Chem. Soc.*(2003, minor revision)之中。

與王念夏教授及陳益佳教授合作部分，也經由雷射瞬態光解偵測到自由基及活性中間體的光譜，並經由與烯類進行的反應動力學，獲得很多有關自由基反應速率的珍貴資料，我們已著手進行整理，將會有完整的另外三篇著作。