

行政院國家科學委員會專題研究計劃結案報告
光與熱化學產生的自由基對與雙自由基之研究

**The Studies of Photo- and Thermo-generated Radical Pairs and
Biradicals**

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主持人：鍾文聖 國立交通大學應化系 wschung@cc.nctu.edu.tw

一、中文摘要

我們完成了 α 芳基噻吩、吡咯類 sultines 化合物以及 disultines 的合成，這些化合物可以是雙自由基、自由基對或四自由基的前驅物，其構造如計畫書中所示。

在成功合成這些化合物之後，除了與王念夏及陳益佳兩教授合作，進行雷射瞬態吸收光譜及反應動力學之研究之外，也針對上述的各種 sultines 進行光化學反應，並利用自由基捕捉試劑（各式烯類及捕捉後能產生安定自由基的試劑 MNP, DMPO），希望能釐清究竟反應中間體是自由基對或雙自由基。除了產物的分析與鑑定，此類化合物的電子順磁共振光譜 (ESR) 以及低溫介質霍氏紅外光譜的量測，提供了自由基極為寶貴的資訊。

當上述的 sultines 與 C_{60} 進行高溫迴流，很容易脫去 SO_2 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。由這些化合物與控制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，然而我們的重大發現獲致不同的結論。

關鍵詞：雜環鄰萘二烯、自由基對、雙自由基、2,5-雙芳基吡咯、電子自旋共振光譜、霍氏紅外光譜。

Abstract

We have completed the syntheses of several α, α -disubstituted thienosultines, pyrrolisultines, and disultines. These sultines are precursors for radical pairs, biradicals or tetraradicals, as shown in our proposals of 2002.

After successfully synthesizing these compounds, we not only collaborate with Professors N.-S. Wang and I.-Chia Chen to study their transient absorption spectroscopy and kinetics but also study the steady state photochemistry of these sultines in the presence and absence of radical trapping reagents (such as various olefins and MNP, DMPO etc.). We hope, through this work, one may gain strong insights on the involvement of radical pairs or biradicals in the photolysis. Besides traditional product separation and analysis, we also focused on the ESR and Matrix Isolated FTIR of these molecules, which provides valuable information about the reactive radical intermediates.

When heated in the presence of [60]fullerene, the sultines all underwent extrusion of SO_2 and the resulting

heterocyclic-*o*-quinodimethanes were trapped 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 year, we studied the thermolysis and photolysis of a series of 2,5-diaryl-substituted *N*-tosylpyrroles and for the first time, we were able to obtain triplet EPR spectra of these species. The EPR spectra of these sultines and the parent compounds (without the sultine functional groups) reproduced the EPR spectra by J. A. Berson in three JACS papers published in 1997, however, different conclusions are reached from our results!

Keywords: *o*-quinodimethanes, Radical Pairs, Biradicals 2,5-diarylpyrroles, Electron Spin Resonance Spectroscopy, FTIR.

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

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 會先脫去 SO₂ 的小分子，進而生成 non-Kekulé 的雙自由基分子，然後與親雙烯物生成 1:1 的加成產物，產率大致在 50-85% 之間。將 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；不過單純由濃度效應無法區分上述機制何者適用。將 Sultine 與正丁基鋰試劑反應發生親核性開環反應，經由水的處理之後得到亞? 醇產物。另外，將 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.)

將碳六十與微過量的 2,5-雙取代? 吩 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。這與之前本實驗室研究 quinoxaline sultines 之結果相似，請參考拙著：*J. Org. Chem.* **2000**, *65*, 3395。

2,5-disubstituted-thienosultines(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 commercially available Rongalite (sodium formaldehyde sulfoxylate) reagent 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-d₄, 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).

When C₆₀ was refluxed in *o*-dichlorobenzene for a variable period of time with a slight excess of the 2,5-disubstituted thienosultines **5a-d**, the 1:1 cycloadducts were obtained in 53-84% yield. The results with [60]fullerene are similar to those observed for quinoxalino-sultines. For details, please refer to our previous work: *J. Org. Chem.* **2000**, 65, 3395.

四、計劃成果自評

本計劃大部份依原定計劃如期完成，已經發表論文篇如下：(1) *J. Chinese. Chem. Soc.* **2002**, 49, 77 ; (2) *J. Org. Chem.* **2002**, 67, 9267-75。另外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，有兩篇投稿送審之中。

另外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，有兩篇投稿送審之中。

Most of the proposed work are successfully carried out and two papers have been published in related subjects: (1) *J. Chinese. Chem. Soc.* **2002**, 49, 77; (2) *J. Org. Chem.* **2002**, 67, 9267-75. The collaboration work with Prof. Wang and Chen, which is related to laser flash photolysis and kinetics, provides us useful information about the reactive intermediates. Based on the work, two manuscripts have been submitted.