

行政院國家科學委員會專題研究計劃成果報告
以雷射技術研究大氣化學之重要分子-有機硫化物之合成與
光化學(II)-(子計畫四)

Using Laser Techniques in the Study of Important Molecules in
Atmosphere-Oxidation of Sulfur Compounds-The Synthesis and
Photochemistry of Organic Compounds (II). (Subproject No 4)

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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」整合型研究計劃之子計畫四，研究有機硫化物之合成與光化學(II)。

本計畫致力於含 3,4-二亞甲基雜環的新 *sultines* 類化合物的合成，例如 *Quinoxalino-fused sultines* 的合成，以及它們在 *Diels-Alder* 反應上的應用。與陳益佳、王念夏二位教授合作對這些化合物做雷射瞬態光解反應，初步成果顯示我們確實能捕捉到一個活性中間物，這部分成果已於進度報告中演講，目前尚待理論計算之驗證即可投稿。部份合成的成果已發表於 *Chem. Commun.* **1997**, 205。未來我們仍期望能對這些含硫有機化合物的反應機制有更深入的瞭解。

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%。變溫的氫核磁共振光譜顯示上述的碳六十加成產物之亞甲基具有動態平衡。其船形至船形的構形翻轉之活化能與其它相關非雜環化合物的活化能為小(14.5 至 15.2 kcal/mol)。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。

我們也針對上述的各種 *sultines* 進行

光化學反應，並利用自由基、各種烯或炔類捕捉試劑進行反應，可得到立體專一性的 *Diels-Alder* 加成產物，證實這類 *Sultines* 確實可以用光化學的方法產生活性極高的 *o-quinodimethanes*。

關鍵詞：雜環鄰萘二烯、瞬態吸收光譜法、硫化物、*Diels-Alder* 反應。

Abstract

This project is a joint effort in the application of laser techniques in the study of important molecules in atmosphere -The synthesis of organic sulfur compounds and its photochemistry (II) (subproject no 4).

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 also studied the laser flash photolysis (LFP) of these *sultines*. Preliminary results showed that a reactive intermediate was observed upon LFP, which we reported during the annual progress report. In the future we shall continue in studying the details of the photolysis of *sultines*.

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

and the resulting heterocyclic-*o*-quinodimethanes were intercepted as the 1:1 adducts in 53% to 84% yields. The temperature dependent ¹H-NMR spectra show a dynamic process of the methylene protons. The activation free energies determined for the boat-to-boat inversion (14.5 to 15.2 kcal/mol) are found to be lower than those obtained for other related carbocyclic analogues. Various temperature ¹³C-NMR spectroscopy also provides important information about the structure of cycloadducts and reveals interesting spectra and symmetry correlation.

Keywords: *o*-quinodimethanes, transient absorption spectroscopy, Sultines, Diels-Alder Reaction.

二、緣由與目的

[60]fullerene derivatives have become the current focus of research in biological and material science because of its unique spherical structure and feasibility in bulk production. Among the many derivatization methods available, cycloaddition reactions have played an important role and the Diels-Alder adducts of C₆₀ were first obtained by Müllen et al. using *o*-quinodimethane as diene. These highly reactive species, generated *in situ* from a variety of precursors, are efficiently trapped with [60]fullerene which gain extra stabilization due to the restoration of aromatic system.

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

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.

In summary we have developed a high yield and regiospecific method for the synthesis of quinoxalino-fused derivatives of [60]fullerene. Among the other reported methods, our results give the best yields. Also it is important to note that none of the bis-adducts of [60]fullerene was detected (<1%) in the reaction studied here, which is in sharp contrast with those with *o*-quinodimethane **1**. Quinoxalino-fused sultines are useful synthons of hetero-*o*-quinodimethanes, they react at milder condition and give better yields than

those of corresponding sulfolenes and dibromides.

四、計劃成果自評

本計劃大部份依原定計劃如期完成，可發表論文至少一篇。

五、參考文獻

1. This work has been presented in (a) The 16th International Congress of Heterocyclic Chemistry, Bozeman, Montana, August 10-15, 1997, Book of Abstracts, OP-V-13 and (b) The 216th National Meeting of American Chemical Society, Boston, August, 1998, paper no. 139.
2. 相關的著作：(a) Torres-Garcia, G.; Luftmann, H.; Wolff, C.; Mattay, J. J. *Org. Chem.* **1997**, *62*, 2752; (b) Fernandez-Paniagua, U. M. et al. *ibid*, **1997**, *62*, 3705.