行政院國家科學委員會專題研究計劃進度報告

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(1/3)

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

The Cycloaddition of Sulfur Containing Heterocycles with C-60 and their photolysis 1/3).

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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

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**(1/3)。

本實驗室過去多年以來從事許多含硫雜環化合物的合成，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，這部分計畫已經和陳益佳(**清大**)**及本所王念夏二位教授合作一段時日。目前我們已成功的建立雷射瞬態吸收光譜儀，並開始偵測上述的活性自由基與中間物，已看到幾個化合物的** transient absorption **光譜，正在進行相關的動力學量測之中。**

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。**

關鍵詞：雜環鄰苠二烯、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 cycloaddition of sulfur containing heterocycles with C-60 and their photolysis (1/3).

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 also studied the laser flash photolysis (LFP) of these sultines. Preliminary results showed that reactive intermediates were observe upon LFP. We are studying their detailed kinetics with the trapping experiments with diylophiles.

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 ^{1}H-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 ^{13}C-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 C_{60} 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 SO_2 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 ℃ in contrast with the high reactivity of corresponding sultines.

When C_{60} 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, 最近已經發表論文一篇：*J. Org. Chem.* **2000**, *65*, in press (paper no. JO9918448)。

附註： 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.