

Photochemical and Thermal Oxidations of 1-Methylthianthrene

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There is considerable interest in photooxygenation of organic sulfides, especially by singlet oxygen and the reactions continues to yield intriguing results about their structures and the reactivities of peroxidic intermediates.¹ The products in these reactions were sulfoxides, sulfones, disulfides, and sulfinate which were varied depending upon the solvents. Some years ago, we reported the result of photooxidation of thianthrene (1) in which thianthrene 5-oxide (2), thianthrene 5,10-dioxide (3), thianthrene 5,5-dioxide (4), and 1,2-benzenedisulfonate (5) were obtained as products.

The isolation of 5 as a major product, to our knowledge, was the first example demonstrating the formation of a sulfonate from the photooxidation of a sulfide. So it seemed to be a promising method to synthesize various 1,2-benzenedisulfonates from thianthrene derivatives. We undertook the investigation of photooxidation of 1-methylthianthrene (6) in order to see the substituent effects and possibly obtain some information about the intermediate involved in the photooxidation of 1. Here is the result on the photooxidation of 6 and the result is compared with that of the thermal oxidation of the same compound.

The experimental procedure for the photooxidation of 6 was followed by the method for that of 1.² 1-Methylthianthrene (966 mg, 4.194 mmol) was dissolved in acetonitrile (430 ml), followed by the addition of aqueous sodium hydroxide (30%, 20 ml), which was irradiated for 4h at 15 °C. Oxygen gas was bubbled through the reaction. The reaction mixture was worked up as usual, and the residue was chromatographed in a series as described: Elution with *n*-hexane (120 ml) gave 6 (96 mg, 0.417 mmol, 9.9%). 1-Methylthianthrene 5,5-dioxide (7, 91 mg, 0.347 mmol, 8.3%); mp 173–174 °C (EtOH); ¹H NMR (CDCl₃, 60 MHz) δ 2.55 (s, 3H, Me), 7.36–7.79 (m, 5H, 2, 3, 7, 8, 9 positions of Ar), 8.11–8.32 (m, 2H, 4, 6 positions of Ar); IR (KBr) 1310, 1100–1200 cm⁻¹; UV λ_{max}^{CH₃CN} 310 (ε, 7,100), 284 (10,900), 262 (13,800), 226 (56,900) nm; MS *m/e* 262 (M⁺), and 1-methylthianthrene 5,10-dioxide (8, 71 mg, 0.271 mmol, 6.5%); mp 101–102 °C (EtOH); ¹H NMR (CDCl₃, 60 MHz) δ 2.55 (s, 3H, Me); 7.21–8.12 (m, 7H, Ar); IR (KBr) 1440, 1250, 1075, 1035 cm⁻¹; UV λ_{max}^{CH₃CN} 280 (ε, 1,750), 236 (12,750) nm; MS *m/e* 262 (M⁺) were obtained from dichloromethane (85 ml). Methanol fraction (150 ml) yielded sodium sulfate (392 mg, 65.8%).

In contrast with the photooxidation of 1, no benzenedisulfonates such as 5 and 3-methylbenzenedisulfonate were detected. The isolation of a large amount of sodium sulfate, which was also an oxidation product of sulfur atom led to the thermal oxidation of 6.

The compound 6 (1,990 mg, 8.639 mmol) was dissolved in acetic acid (100 ml), followed by the addition of hydrogen peroxide (28%, 1.52 ml). The mixture was refluxed for 22h and then cooled to room temperature. Water (60 ml) was added and the mixture was neutralized with sodium carbonate,

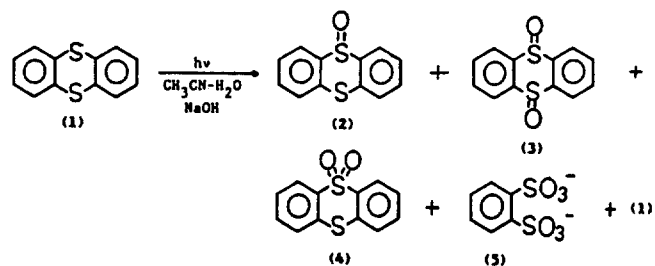


Figure 1.

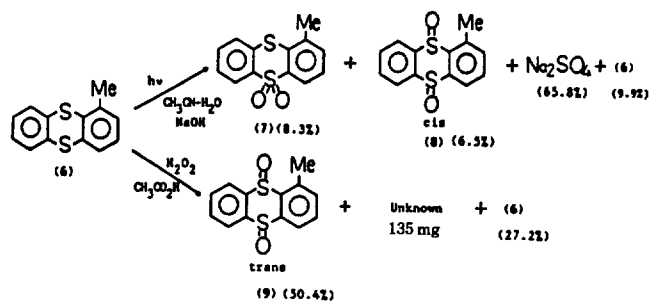


Figure 2.

followed by overnight. White precipitate formed was filtered and chromatographed as in the photooxidation products. From this reaction were obtained 6 (542 mg, 2.353 mmol, 27.2%) and 1-methylthianthrene 5,10-dioxide (9, 1,143 mg, 4.357 mmol, 50.4%); mp 84–85 °C (EtOH); ¹H NMR (CDCl₃, 60 MHz) δ 2.55 (s, 3H, Me), 7.21–8.11 (m, 7H, Ar); IR (KBr) 1435, 1250, 1120, 1070, 1035 cm⁻¹; UV λ_{max}^{CH₃CN} 280 (ε, 2,900), 242 (14,900) nm; MS *m/e* 262 (M⁺).

The structures of all compounds were identified based on the spectroscopic data. Differences between photo- and thermal oxidation reactions lie in the formations of sulfone (7) and a large amount of an inorganic salt in the former and a unknown compound, of which structure has not been identified, in the latter. In addition, although 1-methylthianthrene 5,10-dioxides (8, 9) were formed in both reactions, they appeared to be different. In fact, they are geometrical isomers. The structural assignment of two isomers was made by the analogy with those of *cis*- and *trans*-thianthrene 5,10-dioxides (3). That is, *cis*-(3) has higher mp (283–284 °C) than *trans*-(3) (248–248.5 °C)³ and it has been known that *cis*-(3) shows UV maximum absorption at shorter wave length than *trans*-(3) by less than 10 nm.⁴ Furthermore, configurational analysis of 3 by IR has been also studied.⁵ The S–O stretching frequency of *cis* isomer appeared to be higher than *trans* isomer. In view of the data on 3 and 8 formed by photooxidation was assigned to be *cis* form and 9 formed by thermal oxidation was assigned to be *trans* isomer.

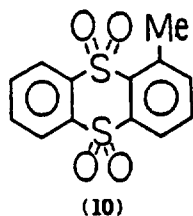


Figure 3.

Thermal isomerization from *trans*-(3) to *cis*-(3) has been reported to occur at 200 to 300 °C.⁴ However, the corresponding isomerization of 9 did not occur at 160 °C to 180 °C at which temperature 9 sublimed.

When a large excess amount of hydrogen peroxide was used (6, 3.038 mmol, H₂O₂, 5 ml, 4h), 1-methylthianthrene 5, 5, 10, 10-tetroxide (10); mp 297–298 °C (CH₃CO₂H); ¹H NMR (DMSO-*d*₆, 100 MHz) δ 2.80 (s, 3H, Me), 7.82–7.97 (m, 4H, 2, 3, 7, 8 positions of Ar), 8.05–8.42 (m, 3H, 4, 6, 9

positions of Ar); IR (KBr) 1450, 1320–1150 (br) cm⁻¹; UV λ_{CH₃OH}^{max} 294 (ε, 8,200), 284 (9,200) nm; MS *m/e* 294 (M⁺), was obtained in 56% yield. It was unsuccessful to detect either sulfone or trioxide of 6.

Acknowledgement. This work was supported by a grant from Dae Woo Foundation.

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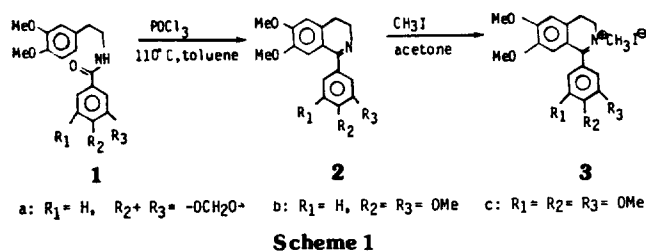
Enantioselective Synthesis of Cryptostyline I, II and III via Asymmetric Reduction

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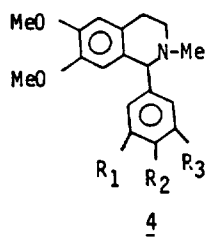
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Since the first naturally occurring 1-substituted phenyl-2-methyl-1,2,3,4-tetrahydroisoquinoline alkaloids, cryptostyline I, II and III, (4a, 4b and 4c, respectively) were isolated from *orchidaceae*, much efforts for the structural elucidation of 4 have been devoted.^{1,2} However, no attempts of enantioselective synthesis of 4 have not been made.³

Recently a wide variety of high promising chiral reducing agents achieving excellent optical induction for prochiral ketones have been developed.⁴ Among them, it was realized that chiral boron and aluminum hydrides, such as K glucoride⁵ 5, Itsuno's reagent⁶ 6 and Mosher's reagent⁷ 7 provide high optical inductions for asymmetric reduction of imine derivatives.^{6,8} The compound 4 could be obtained by reduction of the corresponding iminium salts 3^{1b,9} Therefore, it appeared desirable to undertake the study of enantioselective



synthesis of 4 by asymmetric reduction 3 using these hydrides. This paper describes the results. The requisite iminium salts 3 could be readily prepared by Bischler-Napieralski cyclization of amides 1 with phosphorus oxychloride¹⁰, followed by quaternization with methyl iodide. (Scheme 1). The reaction conditions for reductions were initially chosen to mimic those found most successful for reduction of ketones with the reagents. Thus, the reaction with K glucoride 5 was carried out in THF at -78 °C. The reduction proceeded to completion within 6 h, giving cryptostyline 4 in the range of 80–86% yield. The asymmetric inductions afforded 37% ee for 3a, 43% ee for 3c and 25.2% ee for 3c. Both 4a and 4b obtained are enriched with the *S* enantiomers, which are produced by *re face* attack of hydride. However, the opposite *R* enantiomer is given for 4c. Itsuno's reagent 6 provides somewhat low optical inductions (13–21.1% ee) enriched with the opposite configurations in comparison to those produced by 5. Mosher's reagent 7 gave



- a: R₁ = H, R₂ + R₃ = -OCH₂O-
b: R₁ = H, R₂ = R₃ = OMe
c: R₁ = R₂ = R₃ = OMe