

Stereospecific Conrotatory Ring Opening of a Tetraaryl Thiirane Cation Radical

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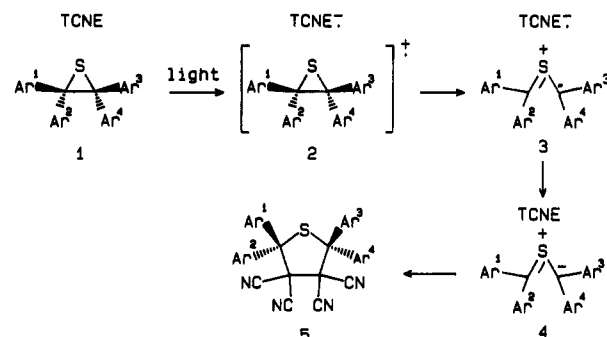
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Orbital symmetry control of electrocyclic reactions has been extensively documented for systems with paired electrons.¹ This communication presents the first example illustrating such control in systems with an unpaired electron.

Kamata and Miyashi² reported that irradiation of the charge-transfer complexes of 2,2,3,3-tetraarylthiiranes **1a–c** and tetracyanoethylene (TCNE) in CH₂Cl₂³ provides cycloaddition products **5a–c** in quantitative yield. They propose the mechanism shown in Scheme 1 in which irradiation induces electron transfer. The thiirane cation radicals **2** thus formed ring open to cation radicals **3**. Back electron transfer from TCNE anion radical to ring-opened cation radical **3** generates thiocarbonyl ylides **4**, which undergo 1,3-dipolar cycloaddition with TCNE to provide cycloadducts **5**. All of these steps occur in a cage because oxygen has no effect on the reaction.² Although the thiirane cation radical is known to be a ring-closed sulfur cation radical,⁴ it is reasonable to expect that aryl substituents favor ring opening.

To determine the stereochemistry of the ring opening of cation radical **2** to **3**, *cis*- and *trans*-tetraarylthiiranes **1d** and **1e**, respectively, were prepared. Reaction of *p*-methoxythiobenzophenone⁵ with phenyl(*p*-methoxyphenyl)diazomethane⁶ afforded thiiranes **1d** and **1e** as a 1:1 mixture.⁷ Fractional recrystallization of this mixture provided one isomer free of its diastereomer and the other as a 90:10 mixture. The structure of the isomer which could be obtained pure was unequivocally determined as the *trans* isomer **1e** by X-ray crystallographic analysis. An ORTEP drawing of this molecule is shown in Figure 1. Both *cis* and *trans* thiiranes **1d** and **1e** form charge-transfer complexes with TCNE in dichloromethane.⁸ Irradiation⁹ of either of these complexes at room temperature gives cycloadducts **5** as the same 3:2 mixture of isomers.¹⁰ Thus there is very modest

Scheme 1. Mechanism for the Photocycloaddition of Tetraarylthiiranes **1** and TCNE^a



^a a, Ar¹ = Ar² = *p*-MeOC₆H₄; Ar³ = Ar⁴ = Ph; b, Ar¹ = *p*-MeOC₆H₄, Ar² = *p*-MeC₆H₄, Ar³ = Ar⁴ = Ph; c, Ar¹ = *p*-MeOC₆H₄, Ar² = Ar³ = Ar⁴ = Ph; d, Ar¹ = Ar³ = *p*-MeOC₆H₄, Ar² = Ar⁴ = Ph; e, Ar¹ = Ar⁴ = *p*-MeOC₆H₄, Ar² = Ar³ = Ph; f, Ar¹ = Ar² = Ar³ = Ar⁴ = Ph.

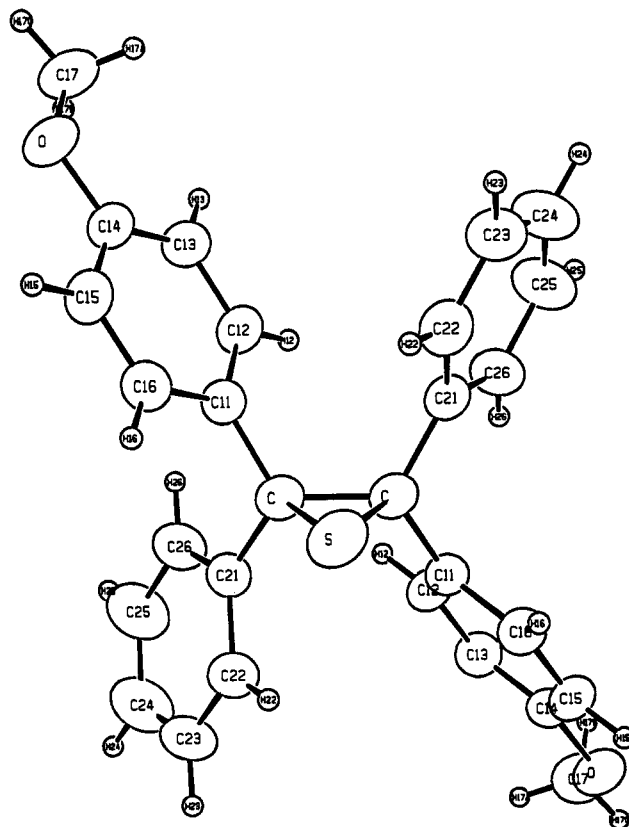


Figure 1. ORTEP drawing of thiirane **1e**.

stereoselectivity¹¹ in this cycloaddition reaction. The isomerization in this reaction occurs during the reaction and not by prior isomerization of the isomeric thiiranes. When the photochemical reaction was allowed to occur to partial completion and the unreacted thiirane reisolated, no detectable isomerization of the thiirane occurred. This is in marked contrast to the well-known photoisomerization of substituted cyclopropanes¹² and oxiranes¹³ via electron transfer. Thus at room temperature the

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(3) Similarly a charge-transfer complex of **1a** and TCNE forms in CHCl₃ and in CH₃CN. Irradiation of the charge-transfer complex in these solvents also gave cycloadduct **5a** in 89% and 75% yields, respectively. A charge-transfer complex between **1a** and TCNE did not form in vinyl chloride, CFC₃, THF, DMSO, EtOH, or Et₂O as solvents.

(4) (a) Qin, X.-Z.; Williams, F. J. *J. Chem. Soc., Chem. Commun.* 1987, 257. (b) Qin, X.-Z.; Meng, Q.; Williams, F. J. *Am. Chem. Soc.* 1987, 109, 6778.

(5) Ramnath, N.; Ramesh, V.; Ramamurthy, V. *J. Org. Chem.* 1983, 48, 214.

(6) Sugawara, T.; Takeda, H.; Izuoka, A.; Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* 1986, 108, 4272.

(7) Staudinger, H.; Siegart, J. *Helv. Chim. Acta* 1920, 3, 833.

(8) Both isomers show new absorptions in the presence of TCNE at λ_{max} 392 and 532 nm in CH₂Cl₂ which are not present in the spectrum of the thiiranes themselves or TCNE alone but only in the spectrum of solutions containing both thiirane and TCNE. These absorptions are all very broad and similar to those measured for **1a** and TCNE in CH₂Cl₂ except for that at 392 nm for the *trans* isomer **1e** and TCNE which is relatively sharp.

(9) These reactions were done by irradiating the samples in Pyrex vessels using an external 200-W mercury (Xe) arc lamp with Corning Glassworks CS3-75 filter, or two 150-W General Electric Miser outdoor lights as light sources.

(10) The ratio of stereoisomers was determined by ¹H NMR spectroscopic analysis. The products obtained at room temperature could be isolated as a diastereomeric mixture after column chromatography on silica gel in approximately 90% yield. The yields were even higher at lower temperature based on consumed starting material after 70–80% conversion.

(11) The definitions of stereoselective and stereospecific reactions used here are those given in the following: Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; p 436.

(12) Boche, G.; Walborsky, H. M. *Cyclopropane Derived Reactive Intermediates*; Wiley: Chichester, 1990; pp 207–236.

(13) (a) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, pp 233–326. (b) Kumar, C. V.; Chattopadhyay, S. K.; Das, P. K. *J. Chem. Soc., Chem. Commun.* 1984, 1107. (c) Kumar, C. V.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.* 1984, 88, 5639. (d) Inoue, Y.; Yamasaki, N.; Shimoyama, H.; Tai, A. *J. Org. Chem.* 1993, 58, 1785.

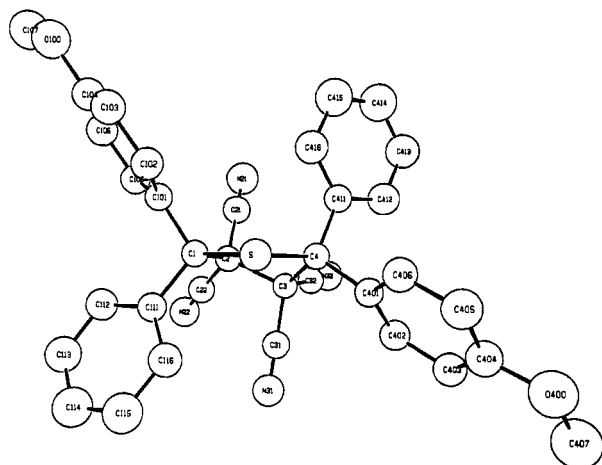


Figure 2. ORTEP drawing of cycloadduct **5e**.

ring-opened cation radical **3** apparently isomerizes thermally before back electron transfer¹⁴ and 1,3-dipolar cycloaddition occurs.¹⁵ Consequently, the reaction was studied at lower temperature. At $-90\text{ }^{\circ}\text{C}$, irradiation of the charge-transfer complex of trans **1e** and TCNE gave cycloadduct **5** as a 2:3 mixture of isomers.¹⁰ Note that this ratio of isomeric products is the reverse of that obtained at room temperature. Irradiation of the charge transfer complex of cis thiirane **1d** and TCNE at $-90\text{ }^{\circ}\text{C}$ produced cycloadduct **5** as a 7:3 mixture of isomers.¹⁰ At $-90\text{ }^{\circ}\text{C}$ this reaction is stereospecific;¹¹ i.e., trans thiirane **1e** yields predominantly one stereoisomeric cycloadduct, and cis thiirane **1d** yields predominantly the other stereoisomeric product. For the stereospecificity of this reaction to be determined, the stereochemistry of cycloadducts **5** must be determined. Fractional recrystallization of the cycloadducts **5** obtained by photocyclization at room temperature afforded in pure form the major stereoisomer produced in this reaction. Crystals suitable for X-ray crystallographic structural analysis were grown, and an ORTEP drawing of the structure determined is shown in Figure 2. This stereoisomer, which is trans, is the minor isomer produced by irradiation of trans thiirane **1e** and TCNE at $-90\text{ }^{\circ}\text{C}$. That is, trans thiirane **1e** forms cis cycloadduct **5d** preferentially and cis thiirane **1d** forms trans cycloadduct **5e** selectively. Since thiocarbonyl ylides are known to typically add in a $\pi_4s + \pi_2s$ fashion,^{16,17} cation radical **2** must ring open to **3** in a *conrotatory* process.¹⁸ These stereochemical results show that disrotatory ring opening of cation radical **2** to **3** is disfavored relative to the conrotatory process. The stereochemical results also argue against concerted cycloaddition of ring-closed cation radical **2** with TCNE anion radical because the geometrically accessible pathway would

produce the opposite stereochemistry to that observed.¹⁹ Although the thiirane cation radical has been studied theoretically,²⁰ the pathway for its ring opening has not. However, oxirane cation radical and its ring opening have been studied theoretically.^{21,22} The 2B_1 state ring opens by a symmetry-forbidden disrotatory process, and the 2A_1 state ring opens by a symmetry-allowed conrotatory process, although more recent calculations suggest that an asymmetric pathway is preferred.

It should be noted that Huisgen and Li reported^{23,24} that tetraphenyl thiocarbonyl ylide **4f**, obtained by decomposition of tetraphenyl-1,3,4-thiadiazoline, could *not* be trapped by TCNE. The only product formed is tetraphenylthiirane (**1f**). However, decomposition of 2,2-bis(*p*-methoxyphenyl)-5,5-diphenyl-1,3,4-thiadiazoline in the presence of excess TCNE afforded cycloadduct **5a** in 50% yield in addition to thiirane **1a**. This result underscores the importance of electronic effects in addition to the steric effects proposed previously^{23,24} in the competition between ring closure of thiocarbonyl ylides to thiiranes and 1,3-dipolar cycloaddition. It also provides a simple rationale for the successful photocycloaddition of **1a** but not **1e** to TCNE.

In sum, our results show that ring opening of cation radical **2** gives **3** preferentially by a *conrotatory* process.²⁵

(17) Examples of two-step 1,3-dipolar cycloadditions of thiocarbonyl ylides have been reported: Huisgen, R. *Advances in Cycloaddition*; Curran, D. P., Ed.; JAI Press: Greenwich, CT, 1988; Vol. 1, pp 1–31. Mloston, G.; Langhals, E.; Huisgen, R. *Tetrahedron Lett.* **1989**, *30*, 5373. Huisgen, R.; Mloston, G. *Tetrahedron Lett.* **1989**, *30*, 7041.

(18) Back electron transfer to ring-opened cation radical **3** from TCNE anion radical produces thiocarbonyl ylide **4**, which undergoes 1,3-dipolar cycloaddition with TCNE to give **5**. Alternatively, ring-opened **3** can react directly with the anion radical to yield cycloadduct **5**. In either case, the electrocyclic ring opening of cation radical **2** is conrotatory. The lack of an observable CIDNP effect (see footnote 19) argues against direct reaction of **3** and TCNE anion radical to form **5**, but stepwise reaction is possible provided that the intermediary zwitterion ring closes before it isomerizes.

(19) Antarafacial addition would give the observed stereochemistry but engenders severe steric interactions. Attempts to observe a CIDNP effect in this reaction, which would substantiate the viability of direct reaction between the cation radical and anion radical leading to product, were unsuccessful. The experiment was done by irradiating a solution of thiirane **1a** and TCNE in CD_2Cl_2 in an NMR tube in an NMR spectrometer cavity while monitoring the ^1H and ^{13}C NMR spectrum of the solution. Monochromatic radiation of 514-nm wavelength from an argon laser conducted by means of a fiber optic into the solution in the NMR cavity was used for the irradiation. Although product absorption peaks were observed in the NMR spectrum on irradiating there was no significant enhanced absorption or emission. For references on the methodology used and its theoretical basis, see: (a) *Chemically Induced Magnetic Polarization*, Lepley, A. R.; Closs, G. L., Eds.; Wiley: NY, 1973. (b) Ward, H. R. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, pp 239–273. (c) Lawler, R. G.; Ward, H. R. In *Determination of Organic Structures by Physical Methods*; Nachod, F. C.; Zuckerman, J. J., Eds.; Academic: New York, 1973; Vol. 5, pp 99–150. (d) Bethell, D.; Brinkman, M. R. *Adv. Phys. Org. Chem.* **1973**, *10*, 53.

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(21) Clark, T. *J. Chem. Soc., Chem. Commun.* **1984**, 666.

(22) Nobes, R. H.; Bouma, W. J.; Macleod, J. K.; Radom, L. *Chem. Phys. Lett.* **1987**, *135*, 78.

(23) Huisgen, R.; Li, X. *Heterocycles* **1983**, *20*, 2363.

(24) Huisgen, R.; Fulka, C.; Kalwinski, I.; Li, X.; Mloston, G.; Moran, J. R.; Pröbstl, A. *Bull. Chem. Soc. Belg.* **1984**, *93*, 511.

(25) The ring opening of thiirane cation radical **2** to **3** is assumed to be a thermal process although a photochemical process resulting in a two-photon reaction has not as yet been rigorously ruled out by light intensity dependence studies. For an overview of multiphoton processes, see: Gedanken, A.; Robin, M. B.; Kuebler, N. A. *J. Phys. Chem.* **1982**, *86*, 4096.

(14) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Goodman, J. L.; Farid, S. *J. Am. Chem. Soc.* **1993**, *115*, 4405.

(15) Facile isomerization of the isomeric ring-opened radical cations obtained by photosensitized isomerization of 2,3-diphenyloxirane has been suggested.^{13b} However, the isomeric carbonyl ylides are believed to be stable and not to equilibrate rapidly.¹³ Analogously at room temperature the isomeric ring-opened cation radicals **3** equilibrate before back electron transfer forms the stable isomeric thiocarbonyl ylides **4**.

(16) (a) Kellogg, R. M. *Tetrahedron* **1976**, *32*, 2165. (b) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*, Padwa, A., Ed.; Wiley: New York, 1984; pp 63–76.