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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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To cite this Article Glass, Richard S. and Jung, Woncheol(1994) 'Mechanism of the Ring Opening of a Tetraaryl Thiirane Cation Radical', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 95: 1, 423 — 424

To link to this Article: DOI: 10.1080/10426509408034261

URL: <http://dx.doi.org/10.1080/10426509408034261>

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MECHANISM OF THE RING OPENING OF A TETRAARYL THIIRANE CATION RADICAL

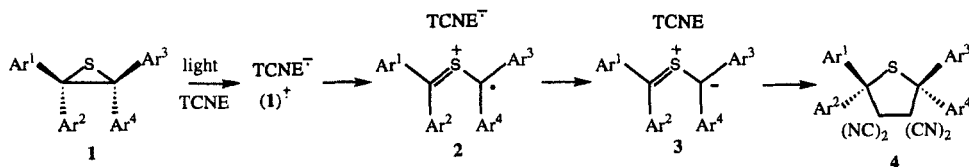
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Abstract The mechanism for the photocycloaddition of tetraarylthiiranes **1** with TCNE was probed by stereochemical and spectroscopic studies. Evidence is presented that the cation radical formed on irradiation of the charge transfer complexes of **1** and TCNE is a *p*-anisyl π -cation radical which then undergoes stereospecific ring opening by C-C bond cleavage.

INTRODUCTION

Irradiation of the charge-transfer complex of thiirane **1a** and tetracyanoethylene (TCNE) in CH_2Cl_2 provides thiolane **4a** in excellent yield.¹ The mechanism suggested for this reaction is first photoinduced electron transfer to generate the thiirane cation



a, $\text{Ar}^1 = \text{Ar}^2 = p\text{-MeOC}_6\text{H}_4$, $\text{Ar}^3 = \text{Ar}^4 = \text{C}_6\text{H}_5$; **b**, $\text{Ar}^1 = \text{Ar}^3 = p\text{-MeOC}_6\text{H}_4$, $\text{Ar}^2 = \text{Ar}^4 = \text{C}_6\text{H}_5$;
c, $\text{Ar}^1 = \text{Ar}^4 = p\text{-MeOC}_6\text{H}_4$, $\text{Ar}^2 = \text{Ar}^3 = \text{C}_6\text{H}_5$

radical and TCNE^- followed by ring opening of $(1a)^{+\bullet}$ with C-C bond cleavage to give **2a**. Back electron transfer from TCNE^- to **2a** results in the formation of thiocarbonyl ylide **3a** and TCNE. 1,3-Dipolar cycloaddition of **3a** and TCNE gives cycloadduct **4a**.

MECHANISTIC STUDIES

Stereochemistry

The stereochemistry of the ring opening of $(1a)^{+\bullet}$ was determined by correlating the stereochemistry of the *cis*- and *trans*-thiiranes **1b** and **1c**, respectively, after photocycloaddition with TCNE with the stereoisomeric thiolanes **4**.² The photocycloadditions were stereospecific at -90° . Irradiation of the charge-transfer complex of *cis*-

thiirane **1b** and TCNE yielded preferentially *trans*-thiolane **4c**; whereas, *trans*-thiirane **1c** preferentially afforded *cis*-thiolane **4b**. Consequently, $(1)^+$ preferentially undergoes *conrotatory* ring opening.

Gamma Radiolysis

To provide insight into the structure of $(1)^+$, the cation radical of thiirane **1a** was generated by gamma radiolysis of thiirane **1a** in CFCl_3 at liquid nitrogen temperature and ESR spectrum measured. This ESR spectrum is shown in Figure 1 and consists



FIGURE 1 ESR spectrum of $(1a)^+$ in CFCl_3 at 77 K.

of a broad absorption with $w_{1/2}=8\text{G}$ and g_{av} of 2.0032. Since g_{av} for thiirane cation radical³ is 2.019 as expected for a sulfur based cation radical, $(1a)^+$ is not a sulfur centered cation radical. However, its g -value and lack of large hyperfine splitting ($a_H < 5\text{G}$) suggests that it is a *p*-anisyl π -cation radical.⁴

Charge-Transfer Complex

Thiiranes **1a-c** and TCNE in CH_2Cl_2 , have two new broad absorption bands in the UV/VIS region, not present in the spectra of the components alone, with λ_{max} at 532 and 392 nm. These absorptions are in the range of the two bands observed in the charge-transfer complexes of anisole and its derivatives with TCNE.⁵ Consequently, it is reasonable to infer that **1a-c** form charge-transfer complexes with TCNE involving complexation of the *p*-anisyl moieties with TCNE.

The cation radical formed from **1a** by gamma radiolysis is a *p*-anisyl π -cation radical and the charge transfer absorptions measured in solutions of thiiranes **1a-c** with TCNE can be accounted for in terms of a charge transfer complex between the *p*-anisyl moieties and TCNE. Therefore, it is concluded that $(1)^+$ formed on irradiating the charge-transfer band of thiiranes **1** and TCNE is a *p*-anisyl π -cation radical and it undergoes stereospecific C-C bond cleavage to form **2**.

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