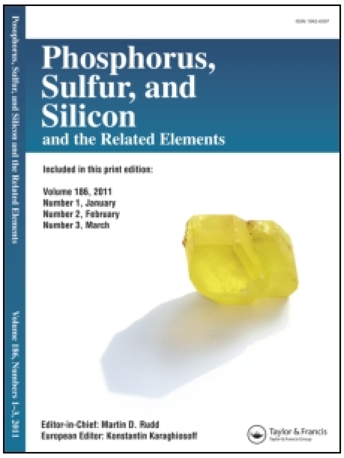

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MECHANISM OF THE RING OPENING OF A TETRAARYL THIIRANE CATION RADICAL

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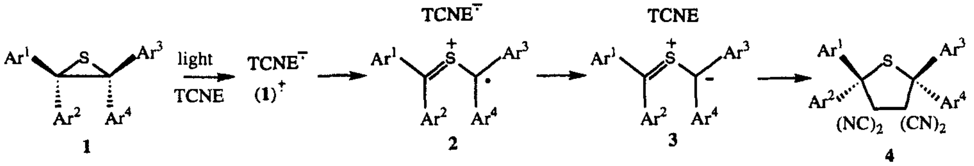
Abstract The mechanism for the photocycloaddition of tetraarylthiiranes **1** with TCNE was probed by stereochemical and spectroscopic studies. Evidence is presented that the cation radical formed on irradiation of the charge transfer complexes of **1** and TCNE is a *p*-anisyl π-cation radical which 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 radical and $TCNE^{\cdot-}$ followed by ring opening of $(\mathbf{1a})^{\cdot+}$ with C-C bond cleavage to give **2a**. Back electron transfer from $TCNE^{\cdot-}$ to **2a** results in the formation of thiocarbonyl ylide **3a** and TCNE. 1,3-Dipolar cycloaddition of **3a** and TCNE gives cycloadduct **4a**.



a, $Ar^1=Ar^2=p\text{-}MeOC_6H_4$, $Ar^3=Ar^4=C_6H_5$; **b**, $Ar^1=Ar^3=p\text{-}MeOC_6H_4$, $Ar^2=Ar^4=C_6H_5$;
c, $Ar^1=Ar^4=p\text{-}MeOC_6H_4$, $Ar^2=Ar^3=C_6H_5$

MECHANISTIC STUDIES

Stereochemistry

The stereochemistry of the ring opening of $(\mathbf{1})^{\cdot+}$ 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, $(1)^{+\cdot}$ preferentially undergoes *conrotatory* ring opening.

Gamma Radiolysis

To provide insight into the structure of $(1)^{+\cdot}$, 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 of a broad absorption with $w_{1/2}=8G$ and g_{av} of 2.0032. Since g_{av} for thiirane cation radical[3] is 2.019 as expected for a sulfur based cation radical, $(1a)^{+\cdot}$ is not a sulfur centered cation radical. However, its g-value and lack of large hyperfine splitting ($a_H<5G$) suggests that it is a *p*-anisyl π-cation radical.[4]

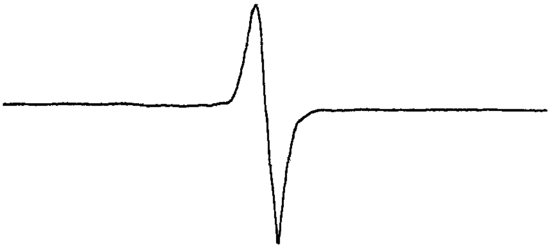


FIGURE 1 ESR spectrum of $(1a)^{+\cdot}$ in $CFCl_3$ at 77 K.

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 $(1)^{+\cdot}$ 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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