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Photochemical Electron-Transfer Generation of Arylthiirane Radical Cations with Tetranitromethane and Chloranil – Some Novel Observations

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The radical cations from 2,2,3,3-tetraphenylthiirane (**1a**), 2,2-bis(4-methoxyphenyl)-3,3-diphenylthiirane (**1b**), and *trans*-2,3-diphenylthiirane (**1c**) have been generated by photoinduced electron transfer (PET) reactions with tetranitromethane [$C(NO_2)_4$] and chloranil (CA). A charge-transfer complexe (CTC) absorption is observed by UV/Vis spectroscopy between thiiranes (**1**) and $C(NO_2)_4$. On the other hand, quenching studies with azulene suggest that the ET reaction occurs between thiiranes and the triplet CA (^{3}CA). The photochemical reaction of the CTC between thiiranes **1** and $C(NO_2)_4$ yields mainly the corresponding alkenes from the fragmentation of the radical-cation intermediate $\mathbf{1}^{\cdot+}$, together with the products derived from nitration on the phenyl rings. However, oxygen transfer to afford the sulfoxides is not found. A marked solvent effect is observed in this reaction, with cage coupling favored in CH_2Cl_2 (nitration derivatives as primary products) and non-cage coupling observed in CH_3CN (the alkene as the primary product). The PET reactions between **1a**–**b** and CA, in the presence of CH_3OH (or another possible oxygen-centered nucleophile), give the ketone derivatives through ring opening, followed by oxidative cleavage. Conversely, under the same experimental conditions, the thiirane **1c** affords only *trans*-stilbene **2c**. This different behavior is ascribed to a different spin density in the corresponding singly occupied molecular orbital (SOMO) of the radical cation. For $\mathbf{1c}^{+\cdot}$, the spin density is concentrated at the sulfur atom, whereas for $\mathbf{1a}^{\cdot+}$ and $\mathbf{1b}^{\cdot+}$, the charge is distributed onto the aromatic rings.
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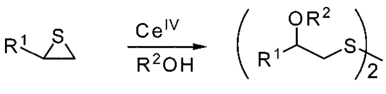
Introduction

Thiiranes or episulfides are three-membered-ring sulfur heterocycles and constitute versatile synthetic intermediates in organic synthesis. New and convenient methods for their preparation have been developed and reviewed.[1] Analogously to oxiranes[2] and aziridines,[3] thiiranes react with nucleophiles under catalytic conditions to give products from ring opening.[4] Thiiranes have also been used advantageously in the pharmaceutical, polymer, pesticide, and herbicide industries.[4] For example, thiirane ring opening by methanesulfenyl bromide results in a halo disulfide which is easily transformed into 2-thioglyceraldehyde, a reported antineoplasic agent.[5]

Studies of thiirane radical cations by EPR spectroscopy,[6a] mass spectrometry,[6b] and theoretical calculations[6c] have provided evidence for dimer formation. The reactivity of the cyclopropane radical cations and their nitrogen and oxygen analogues has been extensively studied; however, there have been only a few studies on the reactivity of thiirane radical cations in solution. Kamata and co-workers have reported the desulfurization of aryl-substituted thiiranes, catalyzed by aminium radical-cation salts, as an efficient preparation of aryl-substituted olefins.[7] Lately, this reaction has been extended to allyl and diallyl thiiranes.[8] In the reaction of *cis* and *trans* diphenyl thiiranes, it has been observed that disubstituted 1,2,3,4-tetrathianes were formed as minor products, thus giving further evidence for the dimerization of the thiirane radical cation.[9] Furthermore, the CTCs of tetraaryl thiiranes and tetracyanoethylene (TCNE) give [3+2] cycloaddition products upon irradiation.[10]

Iranpoor and co-workers have studied the alcoholysis and acetolysis of thiiranes with cerium(IV)[11] and iodide[12], which yielded the corresponding β-substituted disulfide derivatives [Equation (1)]. However, to date, there appear to be no examples in the literature of the reaction of photochemically generated thiirane radical cations with nucleophiles.



(1)

We have previously studied the generation and reactivity of sulfide radical cations in photochemical reactions with $C(NO_2)_4$.[13] These reactions proceed through the initial formation of a CTC followed by light-induced dissociative ET, leading to a triad of reactive species consisting of a sulfur-

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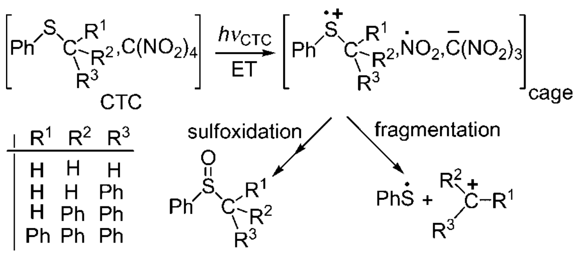
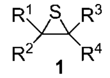
centered radical cation, the radical nitrogen dioxide, and the nitroform anion (Scheme 1). Coupling of the two radicals and subsequent loss of nitrosyl cation give the corresponding sulfoxide (sulfoxidation). Alternatively, C–S cleavage occurs to produce a thiyl radical and a carbocation (fragmentation); the radical dimerizes to the corresponding disulfide, and the cation is trapped by a nucleophile. Competition between *sulfoxidation* and/or *fragmentation* depends markedly on the substrate structure (Scheme 1).



Scheme 1.

CA is a well-established ET photosensitizer, and the ^{3}CA (E_{red} = 2.15 V vs. SCE, in the triplet state) can react at near-diffusion-limited rates with a variety of electron donors.[14] This compound has been used in PET reactions with small-ring hydrocarbons,[15] aziridines,[16] oxiranes,[17] and oxetanes.[18]

This account makes it clear that the study of the chemistry of such novel thiirane (**1a**–**c**, Figure 1) radical cations in solution should be of great interest. In this work we examine the reactivity of thiirane radical cations generated by photochemical ET with $C(NO_2)_4$ and CA, the latter being studied in the presence of CH_3OH. Although the expected β-methoxy disulfide derivatives from ring opening did not occur, a novel fragmentation was observed to afford the ketone derivatives. In comparison, chemical ET (CET) with cerium(IV) ammonium nitrate (CAN) has also been performed.



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1a $R^1 = R^2 = R^3 = R^4 = C_6H_5$
1b $R^1 = R^2 = C_6H_5$, $R^3 = R^4$ = 4-$CH_3OC_6H_4$
1c $R^1 = R^4 = C_6H_5$, $R^2 = R^3$ = H

Figure 1. Structure of the thiiranes employed.

Results

1. Photochemical Reactions of the CTCs between Thiiranes 1 with $C(NO_2)_4$

When $C(NO_2)_4$ was added to a solution of the thiiranes **1a** and **1b** in CH_3CN, a yellow color immediately developed, due to the formation of a CTC, which showed absorption bands as a shoulder between 340–350 nm [Figure 2 and Equation (2)]. These results are in agreement with previously reported data for the CTC between $C(NO_2)_4$ and sulfides.[13]

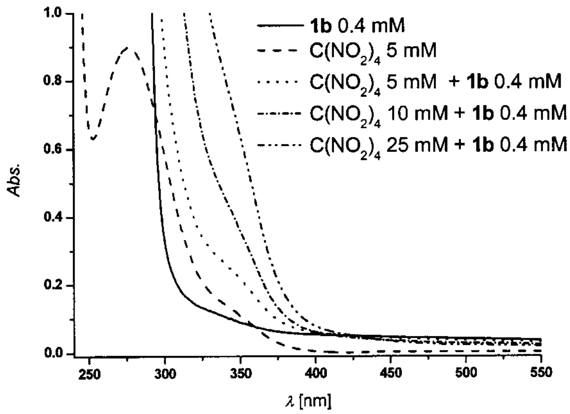
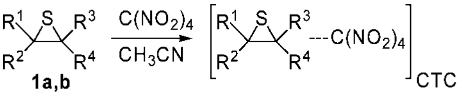
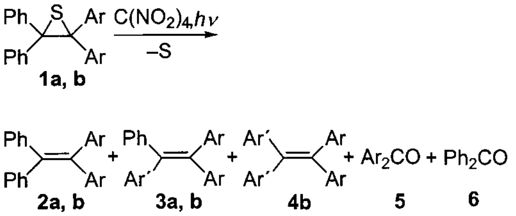


Figure 2. UV/Vis Spectra of Thiirane **1b** and $C(NO_2)_4$ in CH_3CN.



(2)

When a solution of the CTC was kept in the dark under an argon atmosphere, no products were observed. After irradiation of the CTC with a filtered, mercury, high-pressure lamp (150 W, short cutoff filter, λ > 400 nm) and aqueous work-up, the products from desulfurization [Equation (3)] were isolated by silica gel chromatography and identified by spectral analysis (Table 1). The alkene **2a** and the mononitro derivative **3a** were found in comparable yields upon irradiation of the CTC of **1a** with $C(NO_2)_4$. Nevertheless, the photochemical reaction of **1b** with $C(NO_2)_4$ afforded mainly the mononitro alkene **3b**, and as minor products, **2b**, **4b**, and the ketones **5** and **6** (Table 1, entries 1 and 2). In both reactions, elemental sulfur was isolated as a yellow solid and its identity confirmed by mass spectrometry.



(3)

a: Ar = C_6H_5
b: Ar = 4-$CH_3OC_6H_4$
Ar′= 4-$NO_2C_6H_4$

It is known that the desulfurization of thiiranes takes place under irradiation at λ = 230–280 nm.[9] As a control experiment, a 0.1 M solution of **1b** was irradiated at λ > 400 nm, and the thiirane was recovered without decomposition.

When the reaction of **1b** was performed in CH_2Cl_2, only the nitrated alkenes **3b** and **4b** were produced in 33% and 27% yield, respectively, associated with 75% conversion.

Table 1. Photoinduced reaction of thiirane **1** with $C(NO_2)_4$ and control experiments.[a]

Entry	Reactant	Reaction conditions solvent, temp., time	Conversion [%]	*Mb* [%]	Product yield [%] **2**	**3**	**4**	**5**[b]
1[c]	**1a**	CH_3CN, –5 °C, 3 h	64	86	30	20	–	–
2[c]	**1b**	CH_3CN, –5 °C, 3 h	100	78	4	57	17	[d]
3	**1b**	CH_2Cl_2, 20 °C, 2 h	75	100	–	33	27	15
4	**1b**	CH_3CN, 20 °C, 2 h	51	98	16	16	–	17
5[e]	**1b**	CH_3CN, 20 °C, 2 h	43	99	17	15	–	10
6	**2b**	CH_3CN, 20 °C, 2 h	47	99	53[f]	46	–	–
7	**2b**	CH_2Cl_2, 20 °C, 2 h	64	96	36[f]	60	–	–

[a] A solution of **1** (0.1 mmol) and $C(NO_2)_4$ (0.1 mmol) in 5 mL of the solvent was irradiated at $\lambda > 400$ nm under a nitrogen atmosphere; the ketones were quantified by GC and the thiiranes and alkenes by HPLC and ^1H NMR spectroscopy analysis with an internal standard (error 5%). Conversion was determined by quantification of the unreacted thiirane. Mass balance (*Mb*). [b] Together with an equimolar amount of benzophenone (**6**). [c] The product yields were determined through isolation by silica gel chromatography. Elemental sulfur was also isolated in 70–80% yield. [d] Not quantified. [e] Reaction with a $C(NO_2)_4$/**1** of 25:75. [f] Unreacted recovered alkene **2b**.

Also, the *p*-methoxyphenyl ketone (**5**) and benzophenone (**6**) were observed in 15% yield (Table 1, entry 3). A very different product distribution was found when the reaction was conducted in CH_3CN at 20 °C. Thus, the alkene **2b**, the mononitroalkene **3b**, and the ketones **5** and **6** were obtained (Table 1, entry 4). The desulfurization of **1b** also proceeded with substoichiometric amounts of $C(NO_2)_4$, revealing some chain reaction character for these PET reactions (Table 1, entry 5).

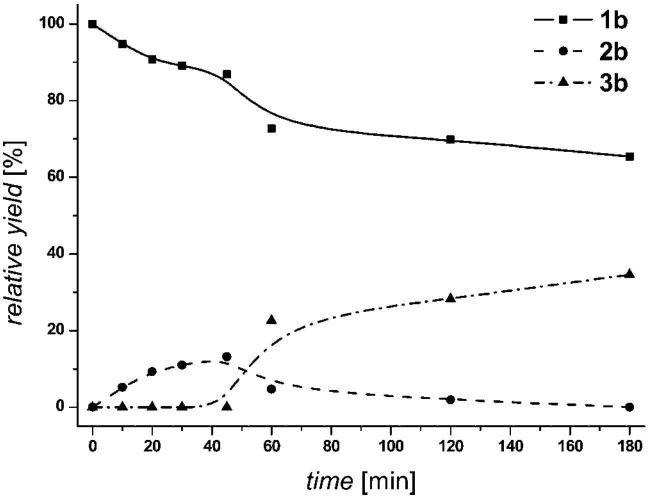


Figure 3. Time profile for the reaction of **1b** with $C(NO_2)_4$ in CH_3CN at 20 °C.

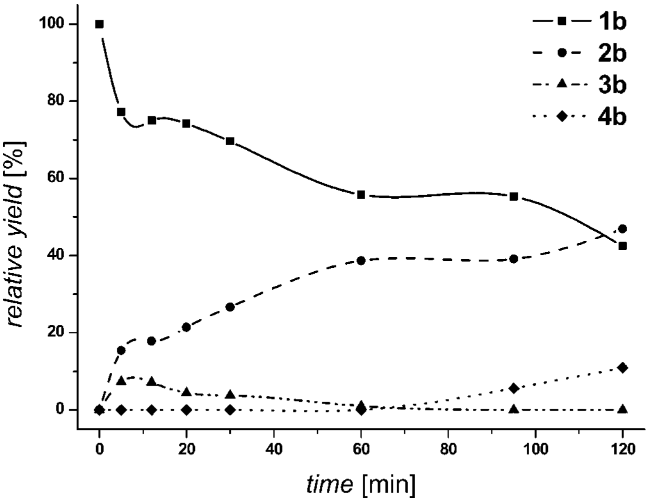
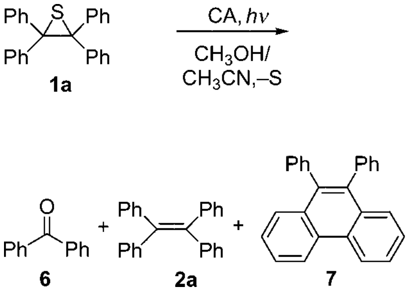


Figure 4. Time profile for the reaction of **1b** with $C(NO_2)_4$ in CH_2Cl_2 at 20 °C.

In order to assess whether **3** is a secondary product derived from **2**, some control experiments were performed. Thus, the alkene **2b** gave the nitro derivative **3b** by a photoreaction with $C(NO_2)_4$ in CH_2Cl_2 or in CH_3CN (Table 1, entries 6 and 7). We have also monitored the reactions of **1b** with $C(NO_2)_4$ in both solvents by HPLC analysis (Figure 3 and Figure 4). While the mononitro alkene **3b** is formed in CH_3CN after 30 min of reaction, in CH_2Cl_2 **3b** is observed almost at the beginning of the irradiation.

2. Photochemical Reactions of Thiiranes with CA in the Presence of CH_3OH

The photochemical reaction of thiirane **1a** with CA as a sensitizer was performed in CH_3CN in the presence of CH_3OH as nucleophile. The main product was benzophenone (**6**), with tetraphenylethylene (**2a**) and 9,10-diphenylphenanthrene (**7**) as minor products [Equation (4)].



(4)

The phenanthrene **7**, isolated from the reaction mixture in <5% yield, was prepared independently by photocyclization of alkene **2a** according to the known procedure.[19]

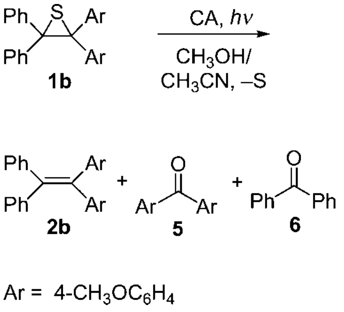
The results of the photochemically induced reactions of thiirane **1b** with CA are presented in Table 2. There was no reaction between thiirane **1b** and CA in the dark in 2 h, since the substrate was quantitatively recovered. When thiir-

Table 2. Photoinduced reaction of thiirane **1b**.[a]

Entry	Reaction conditions λ [nm], solvent, atm., oxidant, additive	Conversion [%]	*Mb* [%]	Product yield [%] **2b**	 **5**	 **6**
1	350, CH_3CN/CH_3OH, N_2, CA	100	99	50	55	43
2	350, CH_3CN/CH_3OH, N_2, CA, azulene[b]	8	100	3	[c]	5.4
3	350, CH_3CN/CH_3OH, O_2, CA	93	80	23	55	46
4	350, CH_3CN/CH_3OH, Ar, CA	90	77	20	49	44
5	350, CH_3CN/CH_3OH, N_2, –	7	100	7	–	–
6	419, CH_3CN/CH_3OH, N_2, –	0	100	–	–	–
7	419, CH_3CN/CH_3OH, N_2, CA	74	91	18	50	44
8	419, CH_3CN, N_2, CA	61	99	37	23	[c]
9	419, CH_2Cl_2/CH_3OH, N_2, CA	86	99	24	61	[d]
10	419, CH_2Cl_2, N_2, CA	88	97	24	61	[d]
11	–, CH_3CN/CH_3OH, N_2, CAN	100	95	50	50	40
12	–, CH_3CN, N_2, CAN	41	100	12	29	[c]

[a] A solution of **1b** (0.4 mmol), oxidant (0.4 mmol) and CH_3OH (80 mmol) in 10 mL of CH_3CN was irradiated with a medium-pressure mercury lamp (maximal emission at λ = 350 nm) or a Rayonet reactor (λ = 419 nm) for 2 h under a nitrogen atmosphere. Ketones were quantified by GC and thiiranes and alkenes by HPLC and ^1H NMR spectroscopy analysis with an internal standard (error 5%). Conversion was determined by quantification of the unreacted thiirane. The average of **5** and **6** was used to evaluate the mass balance (*Mb*). [b] 0.2 mmol. [c] Not quantified. [d] A comparable amount of thiobenzophenone and benzophenone was observed by GC-MS.

ane **1b** was irradiated for 2 h with CA in CH_3CN and in the presence of CH_3OH [Equation (5)], ketones **5** and **6** were obtained, together with the alkene **2b** (Table 2, entry 1).



(5)

The formation of a CTC between the thiirane and CA was not observed by UV/Vis spectroscopy. In the presence of azulene, a known energy-transfer quencher of (^{3}CA),[20] the reaction between **1b** and CA was strongly inhibited (Table 2, entry 2). Furthermore, a control experiment established that no reaction between the thiirane and the azulene took place.

The photoinduced reaction of the thiirane **1b** in the presence of O_2 afforded ketones **5** and **6** in 55% and 46% yield, respectively (Table 2, entry 3). When the reaction was performed under an argon atmosphere (Table 2, entry 4), no significant differences were observed between the results of this reaction and those of the reaction performed under a nitrogen or oxygen atmosphere (Table 2, entries 1 and 3).

In the absence of the photosensitizer CA, only desulfurization was observed, with the alkene **2b** being formed in a 7% yield (Table 2, entry 5). This photochemical desulfurization was avoided by irradiation at λ = 419 nm. Thus, the reaction of **1b** with CA at λ = 419 nm in the presence of CH_3OH gave a lower yield of **2b** (Table 2, entries 6 and 7). When the photoinduced reaction of the thiirane **1b** with CA was performed in the absence of CH_3OH, the yields of ketones **5** and **6** considerably decreased, while the formation of the alkene **2b** increased (Table 2, entry 8).

In CH_2Cl_2 as solvent, in the presence or absence of CH_3OH, the reaction proceeded with higher conversion. In these reactions, a significant amount of thiobenzophenone was observed by GC-MS analysis before work-up (Table 2, entries 9 and 10).

The generation of the radical cation of **1b** was unequivocally proven by its CET reaction in CH_3CN/CH_3OH with CAN, a well-known one-electron oxidant ($E_{red} \approx 1.6$ eV vs. SCE).[21] Ketones **5** and **6** were formed in 50% and 40% yield, respectively, in the presence of CH_3OH, and in its absence, a lower conversion and yield of the products were observed (Table 2, entries 11 and 12). The reaction of **1b** with CAN in CH_2Cl_2 proceeded with less than 5% conversion, due to the very low solubility of the cerium salt in this solvent.

On the other hand, the CET of thiirane **1b** with the tris(4-bromophenyl) hexachloroantimonate aminium salt rendered quantitatively only the alkene **2b** in CH_3CN or in CH_2Cl_2, without any traces of ketones **5** and **6**. Similar results have been previously reported as a convenient method for the desulfurization of thiiranes.[7,8]

The photochemical reaction of **1b** with CA in the presence of CH_3OH was monitored by GC-MS analysis every 30 min. Ketals **8** and **9** were observed as well as minor amounts of the thioketones **10** and **11** (Figure 5). The latter products were hydrolyzed after work-up to the respective ketones **6** and **5**.

Alkene **2b** was proven to be stable under irradiation in the presence of CA and CH_3OH (the same experimental conditions as those used for the photoreactions with thiiranes) and in the presence of CAN. After 2 h of irradiation, alkene **2b** was quantitatively recovered.

Finally, the reaction of the thiirane of *trans*-stilbene **1c** with CA in the presence of CH_3OH gave only *trans*-stilbene (**2c**) in 51% yield without cleavage or dimerization products being observed [Equation (6)].

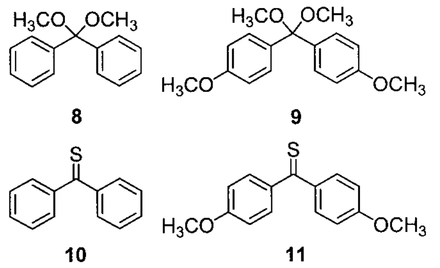
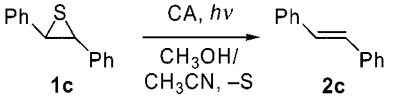


Figure 5. Products from the reaction of **1b** with CA.



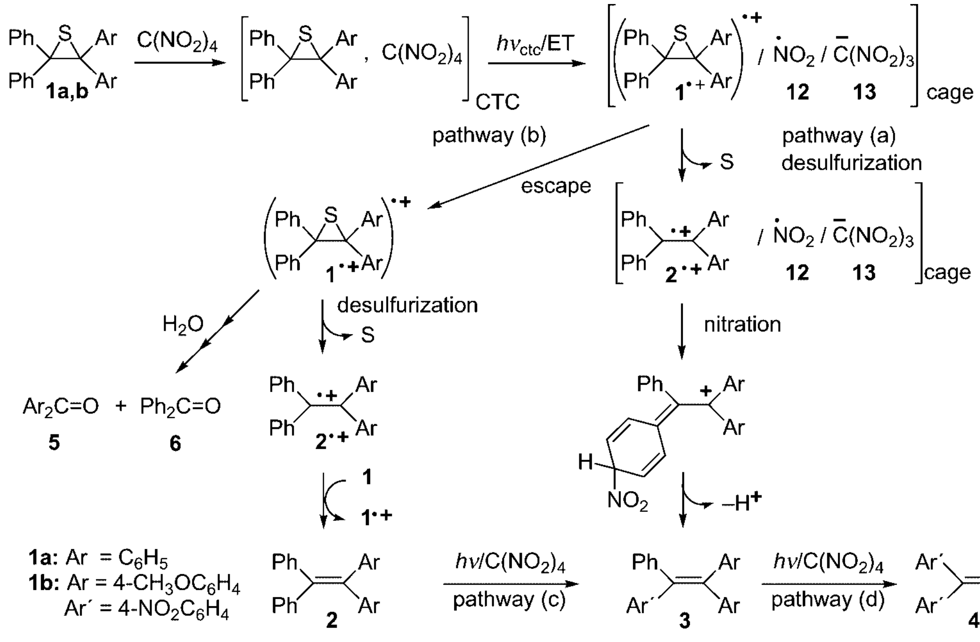
(6)

Mechanistic Discussion

Photochemical ET of Thiiranes with $C(NO_2)_4$

The products observed in the photochemical reaction of the CTC between thiiranes **1** and $C(NO_2)_4$ (Table 1) may be readily rationalized in terms of the thiirane radical cation $\mathbf{1}^{\cdot+}$, generated by a PET process together with nitrite radical (**12**) and the nitroform anion **13** (Scheme 2). The radical cation $\mathbf{1}^{\cdot+}$ has two reaction possibilities. Pathway (a) involves C–S fragmentation and desulfurization in the solvent cage to yield the alkene radical cation $\mathbf{2}^{\cdot+}$. This radical cation finally renders the nitroalkene derivative **3** after geminate coupling with the radical **12** and deprotonation. In pathway (b), fragmentation and desulfurization after escape from the solvent cage occur with the formation of the alkene radical cation $\mathbf{2}^{\cdot+}$, which by ET[22] with the thiirane **1**, yields the alkene **2**. The newly generated radical cation $\mathbf{1}^{\cdot+}$ engages in a chain reaction. This accounts for the catalytic behavior partly observed in this reaction, since the nitro derivative **3b** required two moles of $C(NO_2)_4$ (pathways b–c). Ketones **5** and **6** are probably generated by ring opening of the radical cation $\mathbf{1}^{\cdot+}$ followed by reaction with water present in trace amounts in CH_3CN or the nitroform anion in CH_2Cl_2, (for further discussion of this reaction pathway, see below). The nitroalkenes **3** and **4** [Equation (3)] can also be formed by further oxidation of the alkene **2** by $C(NO_2)_4$ [Scheme 2, pathway (c) and (d)].

A marked solvent effect was observed in the PET reaction of **1b** with $C(NO_2)_4$, by monitoring the reaction in both CH_3CN and CH_2Cl_2 at 20 °C. In CH_3CN, the reaction proceeded with formation of the alkene **2b** as a primary product and nitro derivative **3b** as a secondary product from further reaction with $C(NO_2)_4$ [Scheme 2, pathways (b) and (c)]. In contrast, the reaction in the non-polar CH_2Cl_2 yielded the mononitro derivative **3b** as a primary product by coupling of the nitrogen dioxide radical with $\mathbf{2b}^{\cdot+}$ within the solvent cage and further deprotonation [Scheme 2, pathway (a)]. The experimental results show that the nitration of the phenyl rings is more effective in CH_2Cl_2 than in CH_3CN under the same conditions (Table 1, entries 3 and 4). Temperature also affects the mechanism of this reaction by changing the viscosity of the solvent. When the reaction was conducted in CH_3CN at –5 °C, a cage reaction was favored, due to a higher viscosity of the solvent, and the ratio of products was more similar to that found in CH_2Cl_2,



Scheme 2.

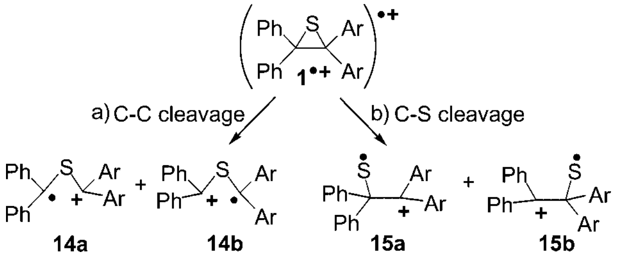
(Table 1 entries 2 and 3). On the other hand, in CH_3CN at 20 °C, out-of-cage products were observed (Table 1, entry 4).

Photochemical Ring Opening Induced by CA in the Presence of CH_3OH

The photochemical reaction between **1** and CA proceeded by an ET pathway between ^{3}CA and the thiirane with concomitant generation of $\mathbf{1}^{\cdot+}$, as confirmed by the inhibition experiments with azulene (triplet energy quencher).[20] Surprisingly, these reactions afforded the diaryl ketones as the main products instead of the expected 2-methoxythiol or disulfide derivatives as products ring opened by CH_3OH.[11,12] The formation of ketones by the reaction of the radical cation $\mathbf{1}^{\cdot+}$ through a photo-oxygenation mechanism[23] can be ruled out, based on the following facts. Practically the same results were obtained when the photoreaction was performed under either a nitrogen, argon, or oxygen atmosphere. Ketals and thioketones **8–11** were detected.

While the ring opening of alkyl-substituted thiirane radical cations by alcohols has been reported to afford the disulfides from the 2-alkoxythiol derivatives [C–S fragmentation, Equation (1)],[11,12] evidence for C–C cleavage for tetraarylthiirane radical cations was obtained from the cycloadducts formed in the photochemical reaction with TCNE.[24] In that reaction, a C–C cleavage afforded a radical-ion pair consisting of the thiocarbonyl ylide radical cation and the TCNE radical anion. Back ET occurred, and the thiocarbonyl ylide formed was captured by the TCNE inside the solvent cage to yield a cycloaddition product.

On the basis of the previously reported data, the possibility of an initial C–S or C–C cleavage should be considered for the reaction of thiiranes **1a** and **1b** with CH_3OH (Scheme 3). The most likely process for the radical cations $\mathbf{1a}^{\cdot+}$ and $\mathbf{1b}^{\cdot+}$ is an initial C–S cleavage to afford the distonic radical cation **15**,[25] taking into consideration the lower bond dissociation energy of a C–S versus that of a C–C, the instability of the thiocarbonyl ylide radical cation **14**, which rapidly collapses to a thiirane in the absence of a dipolarophile[10] and the fact that desulfurization is observed as a competitive pathway. Thus, for the ring opening of the tetraaryl-substituted thiiranes under study, a unimolecular pathway is favored, leading to the intermediate **15**, which bears a stabilized diaryl-substituted carbocation and a thiyl radical. The nucleophilic substitution reaction of an arylcyclopropane radical cation is recognized as a three-electron S_N2 reaction,[26] and a similar CH_3OH-assisted ring opening of an oxirane radical cation has been assumed.[27] Yet, previous results of the reaction of thiirane radical cations generated by CAN have shown that substitution with CH_3OH occurs at the more substituted carbon atom, suggesting a non-concerted pathway.[11,12] Furthermore, stereochemical evidence for a unimolecular pathway has been provided in the fragmentation of 1-phenylethyl phenyl sulfide radical cation.[28]

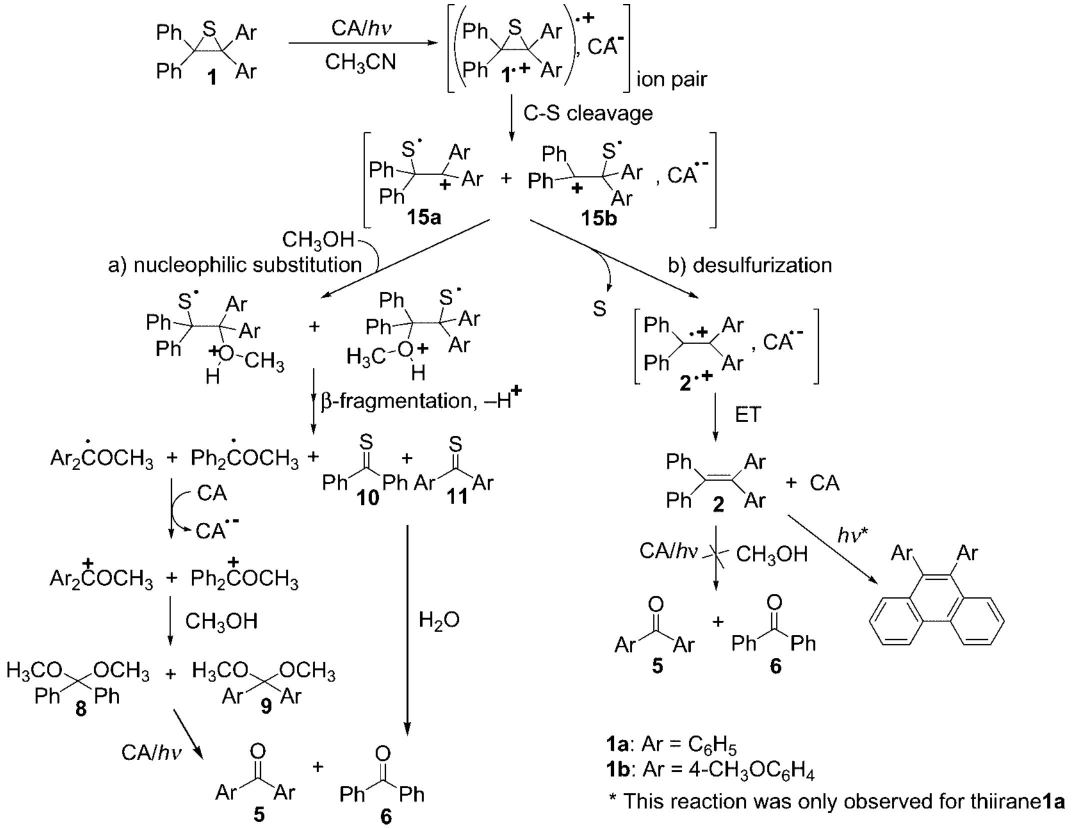


Scheme 3.

The mechanism outlined in Scheme 4 is proposed to account for the results herein obtained. After ring opening of the thiirane radical cation, two possibilities can be envisaged: a) nucleophilic substitution or b) desulfurization. In view of the observed products **8–11**, reaction with CH_3OH may take place on both carbon atoms (pathway a); β-fragmentation of the thiyl radical (C–C cleavage) affords thioketones and new carbon-centered radicals. Further oxidation of the latter and reaction with CH_3OH yield dimethyl ketals **8** and **9**.[29] Photoinduced deprotection of ketals by CA[30] and a water work-up affords the observed ketones **5** and **6**. In the absence of CH_3OH or another oxygen-centered nucleophilic species such as the residual water present in the CH_3CN solvent, $CA^{\cdot-}$ or NO_3^- should also be responsible for the formation of the ketones.[31] This statement is clearly supported by the absence of the ketones in the reaction of thiirane **1b** with the aminium salt in CH_2Cl_2. Under these conditions, there is no nucleophilic species able to afford the ketones. Finally, the stability of the alkene **2b** under irradiation in the presence of CA and CH_3OH or in the presence of CAN suggests that **2b** is not an intermediate in the generation of ketones **5** and **6**. Thus, after desulfurization, the tight ion pair $\mathbf{2b}^{\cdot+}$ and $CA^{\cdot-}$ affords alkene **2b** and CA by ET. This is consistent with the fact that *trans*-4-methoxystilbene[32] and *trans*-anethole[18] were stable in the presence of CA upon irradiation.

The reaction of the thiirane of *trans*-stilbene (**1c**) with CA in the presence of CH_3OH gave only *trans*-stilbene **2c** in 51% yield, without cleavage products being observed. This desulfurization reaction seems to be faster than the nucleophilic substitution by CH_3OH. In order to rationalize these results, we have computed the SOMO coefficients of the thiirane radical cations of **1b** and **1c** by the semiempirical AM1/UHF[33] method.

Figure 6 shows that the SOMO of the radical cation of the *trans*-2,3-diphenylthiirane (**1c**) has the higher spin density on the sulfur atom. In contrast, for the tetrasubstituted thiirane **1b**, the SOMO of its radical cation is localized on the anisyl ring, in agreement with previous data from the EPR spectrum of $\mathbf{1b}^{\cdot+}$. This suggests that it is not a sulfur-centered radical cation but a *p*-anisyl π-radical cation.[34] These preliminary results account for the exclusive formation of the trans-stilbene **2c** from $\mathbf{1c}^{\cdot+}$, whereas $\mathbf{1b}^{\cdot+}$ afforded products from desulfurization (**2b**) and β-fragmentation (**5** and **6**). Presumably, $\mathbf{1c}^{\cdot+}$ desulfurizes directly to afford $\mathbf{2c}^{\cdot+}$ without the formation of the distonic radical cat-



Scheme 4.

ion **15** as an intermediate, as suggested by the localization of spin density mainly on the sulfur atom.[35] For the radical cation $\mathbf{1b}^{\cdot+}$, the spin density distribution on the anisyl moiety strongly supports the formation of a distonic radical cation intermediate **15**, which can account for the competition observed between desulfurization and nucleophilic attack by CH_3OH.

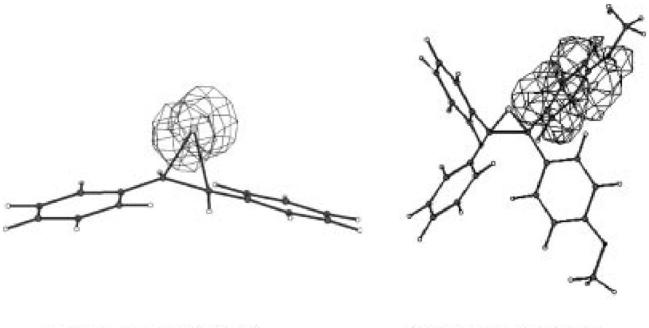


Figure 6. AM1 SOMOs spin density of the thiirane radical cations $\mathbf{1b}^{\cdot+}$ and $\mathbf{1c}^{\cdot+}$.

Conclusions

The electron acceptors $C(NO_2)_4$ and CA generate thiirane radical cations by PET reactions. CTCs between thiiranes **1** and $C(NO_2)_4$ are confirmed by UV/Vis spectroscopy, whereas quenching studies with azulene suggest that the ET reaction occurs between ^{3}CA and thiiranes.

The PET reaction between thiirane **1** and $C(NO_2)_4$ yields products from the radical-cation intermediate through desulfurization, together with products from the nitration of the phenyl rings; sulfoxidation was not observed. Two different pathways may account for the nitrated products, depending on the solvent employed (Scheme 2). For pathway (a) in CH_2Cl_2, nitration within the solvent cage occurs without the alkene as intermediate. However, for pathways (b) and (c) in CH_3CN, the alkene is formed as a primary product. Nitration of the alkene intermediate then takes place as a secondary reaction.

A novel oxidative fragmentation of thiirane radical cations to afford the ketone derivatives is presented herein. These reactions proceed by PET between thiiranes **1b**–**c** and CA. Ketone products are obtained by ring opening followed by reaction with CH_3OH as nucleophile (or another oxygen-centered nucleophilic species), β-fragmentation of the thiyl radical, and further oxidation.

Experimental Section

Methods: The general methods and procedures for the photoinduced reaction are the same as those published before.[13] The reaction products were quantified by GC, HPLC, or ^{1}H NMR with the internal standard method.

Materials: Commercially available compounds were used as received. CH_3CN, CH_2Cl_2, and CH_3OH were distilled under vacuum and stored over molecular sieves (4 Å). The substituted thiiranes were prepared by standard procedures from the thioketones and diphenylcarbene, generated in situ from the diazo derivative[36] or from the reaction of the epoxide with thiourea for the thiirane of the *trans*-stilbene (**1c**).[37] The tris(4-bromophenyl)aminium hexachloroantimonate salt was generated from the triarylamine and $SbCl_5$, according to the literature procedure.[38] All products were characterized by ^1H and ^{13}C NMR spectroscopy and mass spectrometry and exhibited physical properties identical to those reported in the literature.

Photoreaction of Thiiranes with $C(NO_2)_4$ (General Procedure): The photochemical reaction was carried out in a three-necked Schlenk tube equipped with argon- or nitrogen-gas inlets, a condenser with a cooling jacket, and a magnetic stirrer. The tube was dried under vacuum, filled with argon or nitrogen, and loaded with dry CH_3CN (5 mL). To the degassed solvent under an inert atmosphere, thiirane (0.1 mmol) and an equimolar amount of $C(NO_2)_4$ were added. The reaction mixture was cooled to –5 °C and irradiated for 180 min at $\lambda > 400$ nm. The reaction mixture was treated with water (10 mL) and diethyl ether (30 mL). The ethereal layer was separated and submitted to GC, HPLC, and NMR analysis. The products were identified by comparison with authentic samples. Compounds **2b**, **3b**, **4b**, and **5** were isolated by silica gel chromatography with petroleum ether/diethyl ether as the eluent.

Photoreaction of Thiiranes with CA (General Procedure): The photochemical reaction was carried out in a three-necked Schlenk tube equipped with argon- or nitrogen-gas inlets, a condenser with a cooling jacket, and a magnetic stirrer. The tube was dried under vacuum, filled with argon or nitrogen, and loaded with dry CH_3CN (10 mL) and dry CH_3OH (3.25 mL). To the degassed solvent mixture under an inert atmosphere, thiirane (0.4 mmol) and an equimolar amount of CA were added. The reaction mixture was irradiated for 120 min with a medium-pressure mercury lamp (maximal emission at $\lambda = 350$ nm). The reaction mixture was treated with water (10 mL) and diethyl ether (30 mL). The ethereal layer was separated and submitted to GC, GC-MS, HPLC, and NMR analysis. The products were identified by comparison with authentic samples.

1-[2,2-Bis(4-methoxyphenyl)-1-phenylvinyl]-4-nitrobenzene (3b): Compound **3b** was isolated by silica gel chromatography with petroleum ether/diethyl ether (95:5) as the eluent from the ethereal layer of the reaction mixture of **1b** with $C(NO_2)_4$. ^1H NMR (200 MHz, $CDCl_3$, 30 °C): $\delta = 3.74$ (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 6.61–6.66 (m, 4 H, Ar-*H*), 6.89–6.99 (m, 6 H, Ar-*H*), 7.10–7.18 (m, 5 H, Ar-*H*), 7.79 (d, $J = 9.1$ Hz, 2 H, Ar-*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 30 °C): $\delta = 55.39$, 113.37, 113.68, 123.31, 127.01, 128.38, 131.58, 132.36, 132.87, 132.95, 135.48, 135.56, 137.27, 143.42, 143.51, 145.91, 152.06, 158.86, 159.07 ppm. HRMS (EI+): calcd. for $C_{28}H_{23}NO_4$ 437.1627; found 437.1625.

1-[2,2-Bis(4-methoxyphenyl)-4-nitro-1-(4-nitrophenyl)vinyl]benzene (4b): Compound **4b** was isolated by silica gel chromatography with petroleum ether/diethyl ether (80:20) as the eluent from the ethereal layer of the reaction mixture of **1b** with $C(NO_2)_4$. ^1H NMR (200 MHz, $CDCl_3$): $\delta = 3.77$ (s, 6 H, OCH_3), 6.67 (d, $J = 8.8$ Hz, 4 H, Ar-*H*), 6.91 (d, $J = 8.8$ Hz, 4 H, Ar-*H*), 7.14 (d, $J = 8.8$ Hz, 4 H, Ar-*H*), 8.00 (d, $J = 8.8$ Hz, 4 H, Ar-*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 30 °C): $\delta = 55.43$, 113.81, 123.69, 132.38, 132.97, 134.48, 134.98, 146.33, 146.58, 150.66, 159.60 ppm. HRMS (EI+): calcd. for $C_{28}H_{22}N_2O_6$ 482.1478; found 482.1478.

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[1] a) W. Adam, R. Bargon, *Chem. Rev.* **2004**, *104*, 251–261, and references cited therein; b) B. Kaboudin, H. Norouzi, *Tetrahedron Lett.* **2004**, *45*, 1283–1285; c) M. Moghadam, S. Tangestaninejad, V. Mirkhani, R. Shaibani, *Tetrahedron* **2004**, *60*, 6105–6111; d) B. Tamami, M. Kolahdoozan, *Tetrahedron Lett.* **2004**, *45*, 1535–1537.

[2] a) C. Bonini, G. Righi, *Synthesis* **1994**, 225–238; b) N. Iranpoor, I. Mohammadpour-Baltork, *Synth. Commun.* **1990**, *20*, 2789–2797; c) M. Shimizu, A. Yoshida, T. Fujisawa, *Synlett* **1992**, 204–206; d) S. Munavalli, D. K. Rohrbaugh, F. J. Berg, F. R. Longo, H. D. Durst, *Phosphorus Sulfur Silicon Relat. Elem. Phosphorus Sulfur Silicon* **2002**, *177*, 215–230, and references therein.

[3] X. E. Hu, *Tetrahedron* **2004**, *60*, 2701–2743.

[4] a) S. R. Harring, T. Livinghouse, in: *Comprehensive Heterocyclic Chemistry II* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford, **1996**; vol. 1A, pp. 241–250; b) W. Ando, N. Choi, in: *Comprehensive Heterocyclic Chemistry II* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford, **1996**; vol. 1A, pp. 173–240; c) G. Capozzi, S. Menichetti, C. Nativi, in: *The Syntheses of Sulphones, Sulphoxides and Cyclic Sulphides* (Eds.: S. Patai, Z. Rappoport), John Wiley & Sons, New York, **1994**; pp. 529–641; d) D. C. Dittmer, in: *Comprehensive Heterocyclic Chemistry* (Ed.: E. D. Lwowski), Pergamon, Oxford, **1984**; vol. 7, pp. 131–184.

[5] M. G. Silvestri, C.-H. Wong, *J. Org. Chem.* **2001**, *66*, 910–914.

[6] a) X.-Z. Qin, Q.-C. Meng, F. Willians, *J. Am. Chem. Soc.* **1987**, *109*, 6778–6788; b) G. Baykut, K. P. Wanczek, H. Hartmann, *Adv. Mass. Spectrom.* **1980**, *8*, 186–193; c) P. M. W. Gill, P. Weatherall, L. Radom, *J. Am. Chem. Soc.* **1989**, *111*, 2782–2785.

[7] M. Kamata, K. Murayama, T. Miyashi, *Tetrahedron Lett.* **1989**, *30*, 4129–4132.

[8] V. Caló, L. López, A. Nacci, G. Mele, *Tetrahedron* **1995**, *51*, 8935–8940.

[9] M. Kamata, K. Murayama, T. Suzuki, T. Miyashi, *J. Chem. Soc., Chem. Commun.* **1990**, 827–829.

[10] M. Kamata, T. Miyashi, *J. Chem. Soc., Chem. Commun.* **1989**, 557–558.

[11] a) N. Iranpoor, J. Owji, S. Iran, *Tetrahedron* **1991**, *47*, 149–154; b) N. Iranpoor, M. Skekarriz, F. Shiring, *Synth. Commun.* **1998**, *28*, 347–366.

[12] N. Iranpoor, B. Tamami, K. Niknam, *Can. J. Chem.* **1997**, *75*, 1913–1919.

[13] W. Adam, J. E. Argüello, A. B. Peñéñory, *J. Org. Chem.* **1998**, *63*, 3905–3910.

[14] S. M. Hubig, M. Bockman, J. K. Kochi, *J. Am. Chem. Soc.* **1997**, *119*, 2926–2935.

[15] a) W. Bergmark, S. Hector, G. Jones II, C. Oh, T. Kumagai, S. Hara, T. Segawa, N. Tanaka, T. Mukai, *J. Photochem. Photobiol., A* **1997**, *109*, 119–124; b) Y. Takahashi, N. Nishioka, F. Endoh, H. Ikeda, T. Miyashi, *Tetrahedron Lett.* **1996**, *37*, 1841–1844; c) H. D. Roth, *J. Phys. Chem. A* **2003**, *107*, 3432–3437.

[16] E. Hasegawa, S. Koshii, T. Horaguchi, T. Shimizu, *J. Org. Chem.* **1992**, *57*, 6342–6344.

[17] a) K. Maruyama, Y. Kubo, in: *CRC Handbook of Organic Photochemistry and Photobiology* (Eds. W. M. Horspool, P.-S. Song), Boca Ratón, FL, USA, **1995**, pp. 375–383; b) E. Hasegawa, M. Kamata, in: *CRC Handbook of Organic Photochemis-*

try and Photobiology (Eds.: W. Horspool, F. Lenci), 2nd ed., Boca Ratón, FL, USA, **2003**, chapter 53, pp. 1–17.

[18] M. A. Izquierdo, M. A. Miranda, *Eur. J. Org. Chem.* **2004**, 1424–1431.

[19] a) F. Mallory, C. Wood, J. Gordon, *J. Am. Chem. Soc.* **1964**, *86*, 3094–3102; b) T. Sato, S. Shimada, K. Hata, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2484–2490. Reactions described for $\lambda <$ 280 nm.

[20] *Handbook of Photochemistry*, S. L. Murov, I. Carmichael, G. L. Hug, 2nd ed., Marcel Dekker, Inc., New York, **1993**, pp. 58 and 64.

[21] V. Nair, L. Balagopal, R. Rajan, J. Mathew, *Acc. Chem. Res.* **2004**, *37*, 21–30.

[22] Similar favorable ET from the alkene radical cation to the thiirane has been previously reported in the catalyzed desulfurization of thiiranes. See ref.[7]

[23] In the photoinduced reaction of **1b** with TCNE, oxygenation of the thiirane to give the corresponding 1,3,4-dioxathiolane did not occur upon irradiation in the polar solvents CH_3CN or nitromethane or in the presence of oxygen. See ref.[10]

[24] R. S. Glass, W. Jung, *J. Am. Chem. Soc.* **1994**, *116*, 1137–1138.

[25] Similar behavior has been reported for oxirane radical cations: pathway a) C–C cleavage and subsequent formation of carbonyl ylide radical cations, which react with dipolarophiles and oxygen, affording tetrahydrofurans and 1,2,4-trioxolanes, respectively; pathway b) C–O cleavage gives the corresponding radical cations, which rearrange to carbonyl compounds or react with nucleophiles to give addition products. See ref.[17b]

[26] J. P. Dinnocenzo, H. Zuilhof, D. R. Lieberman, T. R. Simppson, M. W. McKechney, *J. Am. Chem. Soc.* **1997**, *119*, 994–1004.

[27] J. Kagan, P. Y. Juang, B. E. Firth, J. T. Przybytek, S. P. Singh, *Tetrahedron Lett.* **1977**, *18*, 4289–4290.

[28] E. Baciocchi, E. Fasella, O. Lanzalunga, M. Mattioli, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1071–1073.

[29] For the arylthiirane radical cations, the β-fragmentation of the intermediate thiyl radical is favored over the dimerization reaction which, is the main pathway with alkylthiiranes [Equation (1)].This different behavior is probably due to the C–C bond dissociation energy, which is lower in the arylthiirane than in the alkylthiirane radical cations.

[30] E. Fasani, M. Freccero, M. Mella, A. Albini, *Tetrahedron* **1977**, *53*, 2219–2232.

[31] The formation of both ketones **5** and **6** in the photochemical reaction of **1b** with $C(NO_2)_4$ can be also ascribed to the nucleophilic attack of water on the distonic radical cation **15**.

[32] J.-H. Xu, L.-C. Wang, J.-W. Xu, B.-Z. Yan, H.-C. Yuan, *J. Chem. Soc. Perkin Trans. 1* **1994**, 571–577.

[33] a) M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909; b) Semiempirical calculations were performed with the AM1/UHF method, as implemented in the AMPAC package from the Quantum Chemistry Program Exchange (QCPE), program no. 506.

[34] R. S. Glass, W. Jung, *Phosphorus Sulfur Silicon Relat. Elem.* **1994**, *95–96*, 423–424.

[35] In the alkylthiirane radical cations, the spin density should also be located on the sulfur atom. Nevertheless, these species do not afford the alkene [Equation (1)], probably due to the higher enthalpy change in the formation of the alkene radical cations.

[36] H. Staudinger, J. Siegwart, *Helv. Chim. Acta* **1920**, *3*, 833–840.

[37] R. Ketcham, V. P. Shah, *J. Org. Chem.* **1963**, *28*, 229–230.

[38] W. Schmidt, E. Steckhan, *Chem. Ber.* **1980**, *113*, 577–585.

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