

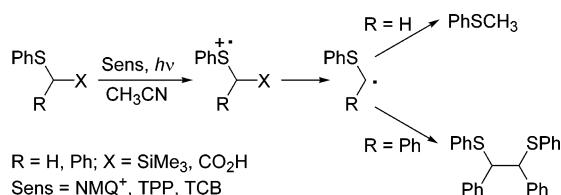
## Sulfur Radical Cations. Kinetic and Product Study of the Photoinduced Fragmentation Reactions of (Phenylsulfanylalkyl)trimethylsilanes and Phenylsulfanylacetic Acid Radical Cations

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Laser and steady-state photolysis, sensitized by  $\text{NMQ}^+$ , of  $\text{PhSCH}(\text{R})\text{X}$  **1–4** ( $\text{R} = \text{H, Ph}$ ;  $\text{X} = \text{SiMe}_3, \text{CO}_2\text{H}$ ) was carried out in  $\text{CH}_3\text{CN}$ . The formation of **1<sup>•+</sup>–4<sup>•+</sup>** was clearly shown. All radical cations undergo a fast first-order fragmentation reaction involving C–Si bond cleavage with **1<sup>•+</sup>** and **2<sup>•+</sup>** and C–C bond cleavage with **3<sup>•+</sup>** and **4<sup>•+</sup>**. The desilylation reaction of **1<sup>•+</sup>** and **2<sup>•+</sup>** was nucleophilically assisted, and the decarboxylation rates of **3<sup>•+</sup>** and **4<sup>•+</sup>** increased in the presence of  $\text{H}_2\text{O}$ . A deuterium kinetic isotope effect of 2.0 was observed when  $\text{H}_2\text{O}$  was replaced by  $\text{D}_2\text{O}$ . Pyridines too were found to accelerate the decarboxylation rate of **3<sup>•+</sup>** and **4<sup>•+</sup>**. The rate increase, however, was not a linear function of the base concentration, but a plateau was reached. A fast and reversible formation of a H-bonded complex between the radical cation and the base is suggested, which undergoes C–C bond cleavage. It is probable that the H-bond complex undergoes first a rate determining proton-coupled electron transfer forming a carboxyl radical that then loses  $\text{CO}_2$ . The steady-state photolysis study showed that  $\text{PhSCH}_3$  was the exclusive product formed from **1** and **3** whereas  $[\text{PhS}(\text{Ph})\text{CH}]_2$  was the only product with **3** and **4**.

### Introduction

In the past decade, the chemistry of sulfide radical cations has continued to attract considerable interest for the theoretical and practical aspects as well as the important biological implications.<sup>1</sup>

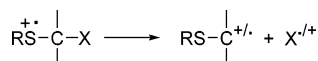
Like most radical cations, sulfide radical cations can undergo a fragmentation process involving the cleavage of a bond  $\beta$  to the positive charge (Scheme 1, where X can be H,  $\text{CR}_3$ ,  $\text{SiR}_3$ ,  $\text{CO}_2\text{H}$ , etc.). This reaction, in general, has interesting implications concerning the structural effects upon the fragmentation rate and mechanism.<sup>2</sup> Moreover, it generally leads to carbon radicals and can also have practical applications.<sup>3</sup> In this respect, it can be mentioned that the process depicted in Scheme 1 can effectively be employed for the photoinitiation of free-radical

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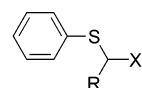
## SCHEME 1



polymerization.<sup>3e</sup> Moreover, it has also been exploited as a mechanistic probe in the enzymatic oxidations of sulfides.<sup>1t,4</sup>

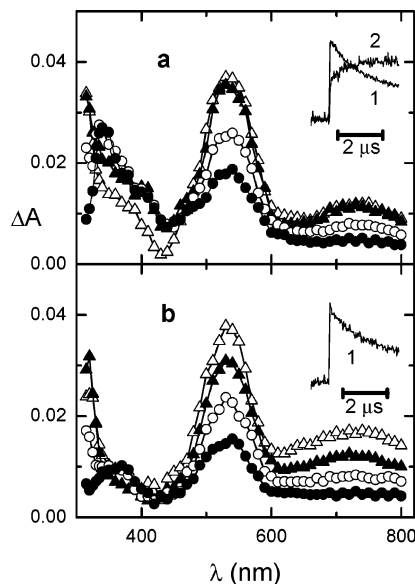
In this context, studies of the fragmentation reactions of sulfide radical cations aimed at acquiring information on the structural effects upon kinetics and mechanism are certainly warranted.

Recently, we have reported a very detailed kinetic study of the fragmentation reactions of 2-arylsulfanyl alcohol radical cations [Scheme 1, X = CH(OH)Ph] that involve the OH-assisted cleavage of a C–C bond.<sup>1c</sup> We have now carried out a kinetic and products study of the fragmentation reactions of the radical cations of silyl sulfides **1** and **2** and the thioacetic acids **3** and **4**.



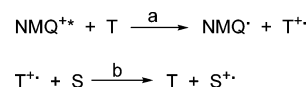
- 1 R = H, X = SiMe<sub>3</sub>  
 2 R = Ph, X = SiMe<sub>3</sub>  
 3 R = H, X = CO<sub>2</sub>H  
 4 R = Ph, X = CO<sub>2</sub>H

The fragmentation reaction involves the cleavage of the C–Si bond in **1**<sup>•+</sup> and **2**<sup>•+</sup> and the cleavage of the C–C bond, with CO<sub>2</sub> loss, in **3**<sup>•+</sup> and **4**<sup>•+</sup>. Some information on the decarboxylation of **3**<sup>•+</sup> has already been reported,<sup>1h</sup> but no kinetic study was carried out. The radical cations **1**<sup>•+</sup>–**4**<sup>•+</sup> were generated by sensitized photolysis, mostly with *N*-methylquinolinium



**FIGURE 1.** Time-resolved absorption spectra of the NMQ<sup>+</sup> ( $1.1 \times 10^{-3}$  M)/toluene (1 M)/**3** ( $1.0 \times 10^{-2}$  M) system in CH<sub>3</sub>CN: (a) N<sub>2</sub>-saturated, recorded 0.016 (Δ), 0.35 (▲), 1.4 (○), and 3.2 (●) μs after the laser pulse and (b) O<sub>2</sub>-saturated, recorded 0.016 (Δ), 0.35 (▲), 1.4 (○), and 3.2 (●) μs after the laser pulse. Insets: decay kinetics recorded at 530 nm (1) and 340 nm (2).  $\lambda_{\text{exc}} = 355$  nm.

## SCHEME 2



tetrafluoroborate (NMQ<sup>+</sup>) as the sensitizer. Fragmentation kinetics were studied by the laser flash photolysis techniques, and products were determined in steady-state photolysis experiments. The results of this study are reported herein.

## Results

**Laser Flash Photolysis Studies.** The laser photolysis experiments were carried out in the presence of 1 M toluene as cosensitizer. Under these conditions, the sequence of reactions a and b, in Scheme 2, takes place (T = toluene and S = sulfide), which leads to a significant increase in the yield of separated radical cations.<sup>5</sup>

Upon laser excitation ( $\lambda_{\text{exc}} = 308$  and/or 355 nm) of CH<sub>3</sub>CN solutions of NMQ<sup>+</sup>/toluene/**1**–**4**, time-resolved absorption spectra and decay kinetics were recorded under N<sub>2</sub>- and O<sub>2</sub>-saturated conditions. Since the results were very similar for all sulfides examined, only those concerning the sulfides **3** and **4** will be illustrated in detail. Absorption maxima and transients observed with the other substrates are reported in the Supporting Information (Table S1).

By laser photolysis of **3** in N<sub>2</sub>-saturated solutions, three absorption bands were detected just after the laser pulse in the 400, 530, and 750 nm regions (Figure 1a). They were assigned to NMQ<sup>•</sup> ( $\lambda_{\text{max}} = 400$  and 550 nm)<sup>6</sup> and the monomer ( $\lambda_{\text{max}} = 530$  nm) and the  $\pi$ -type dimer sulfide radical cations ( $\lambda_{\text{max}} \approx 750$  nm).<sup>11</sup> The time-evolution of the absorption spectra shows that the signal decay recorded at 530 nm is coupled with the growth of a further maximum at 340 nm region assigned to the

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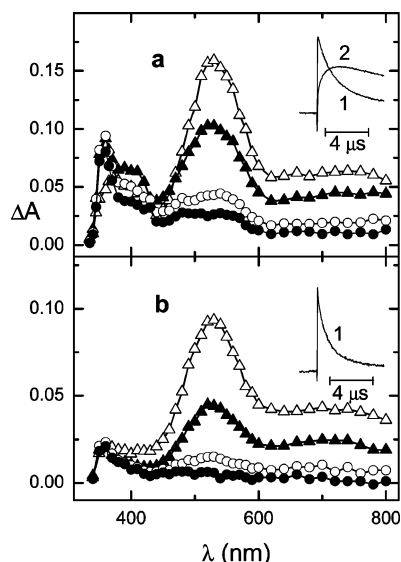
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**FIGURE 2.** Time-resolved absorption spectra of the  $\text{NMQ}^+$  ( $1.1 \times 10^{-3}$  M)/toluene (1 M)/4 ( $9.2 \times 10^{-3}$  M) system in  $\text{CH}_3\text{CN}$ : (a)  $\text{N}_2$ -saturated, recorded 0.032 ( $\Delta$ ), 1.0 ( $\blacktriangle$ ), 3.6 ( $\circ$ ) and 6.4 ( $\bullet$ )  $\mu\text{s}$  after the laser pulse and (b)  $\text{O}_2$ -saturated, recorded 0.032 ( $\Delta$ ), 0.75 ( $\blacktriangle$ ), 2.7 ( $\circ$ ) and 6.4 ( $\bullet$ )  $\mu\text{s}$  after the laser pulse. Insets: decay kinetics recorded at 520 nm (1) and 360 nm (2).  $\lambda_{\text{exc}} = 355$  nm.

absorption of the radical  $\text{PhSCH}_2^\bullet$  (Figure 1a, inset).<sup>10</sup> Accordingly, in  $\text{O}_2$ -saturated solutions, the time-resolved absorption spectra are modified by the fast decay of  $\text{PhSCH}_2^\bullet$  and  $\text{NMQ}^\bullet$  which are efficiently quenched by molecular oxygen; thus, the absorption in the 330–400 nm region decreases and the only recorded transient concerns the radical cation in its monomeric ( $\lambda_{\text{max}} = 530$  nm) and dimeric ( $\lambda_{\text{max}} \approx 750$  nm, Figure 1b) form.<sup>7</sup>

The laser photolysis of **4** gives similar results in terms of absorption bands, time-evolution, and corresponding assignments, both in oxygen- and nitrogen-saturated solutions (Figure 2). Small differences are only in the absorption maximum of the monomer radical cation ( $\lambda_{\text{max}} = 520$  nm) and the radical  $\text{PhSCH}^\bullet\text{H(Ph)}$  ( $\lambda_{\text{max}} = 360$  nm).

The decay rate of radical cations  $1^{+\bullet}$ – $4^{+\bullet}$  was determined by following, in the presence of nitrogen, the decay of the dimer radical cation around 750 nm and, in the presence of oxygen, the absorption decay at about 530 nm (due to the monomer radical cation). In both cases, the decay kinetics followed first-order laws and provided almost identical values for the decay rate constants. With compounds **2** and **4**, in the presence of nitrogen, it was also possible to obtain the decay rate constant of the radical cation from the absorption rise due to the formation of the carbon radical. All values of the first-order rate constants ( $k_{\text{obs}}$ ) are reported in Table 1.

As already observed for the desilylation of aryltrimethylsilane radical cations,<sup>8</sup> addition of nucleophiles, e.g., MeOH, increased the decay rate of  $1^{+\bullet}$  and  $2^{+\bullet}$ . For  $1^{+\bullet}$ , a plot of  $k_{\text{obs}}$  against methanol concentration (Figure 3) was linear affording a second-order rate constant of  $3.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for the MeOH-induced desilylation. With  $2^{+\bullet}$ , the MeOH-induced decay was too fast to be measured.

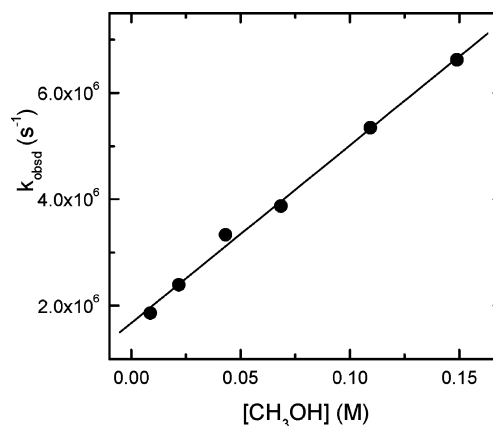
(7) Actually, in the experiments under  $\text{O}_2$ , a transient absorbing below 400 nm is also observed. This transient was not identified, but clearly, there is no link between its formation and the decay of the radical cation that occurs at the same rate than under nitrogen.

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**TABLE 1.** Decay Rate Constants for Fragmentation of the Sulfide Radical Cations  $[\text{PhSCH(R)X}]^{+\bullet}$  in  $\text{CH}_3\text{CN}$

radical cation	additives	$k^a$ ( $10^6 \text{ s}^{-1}$ )
R = H, X = SiMe <sub>3</sub> ( $1^{+\bullet}$ )		1.2
R = Ph, X = SiMe <sub>3</sub> ( $2^{+\bullet}$ )		36
R = H, X = CO <sub>2</sub> H ( $3^{+\bullet}$ )		0.31
R = Ph, X = CO <sub>2</sub> H ( $4^{+\bullet}$ )	H <sub>2</sub> O (2%)	1.6
	H <sub>2</sub> O (5%)	4.1
	H <sub>2</sub> O (2%)	1.1
	H <sub>2</sub> O (2%)	9.3
	D <sub>2</sub> O (2%)	4.5
	H <sub>2</sub> O (5%)	24

<sup>a</sup> Experimental error of  $\pm 10\%$ .



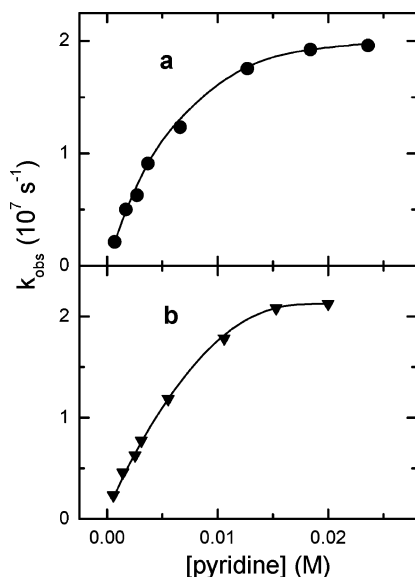
**FIGURE 3.** Observed rate constant for the fragmentation of  $1^{+\bullet}$  vs  $\text{CH}_3\text{OH}$  concentration in  $\text{CH}_3\text{CN}$ .

Interestingly, it was observed that also for the carboxylic acids the first-order decay of the radical cations is significantly accelerated by addition of water. As shown in Table 1, the addition of 5%  $\text{H}_2\text{O}$  (v/v) increases the rate by more than 10 times with  $3^{+\bullet}$  and more than 20 times with  $4^{+\bullet}$ . When  $\text{D}_2\text{O}$  replaced  $\text{H}_2\text{O}$ , the decay rate of  $4^{+\bullet}$  decreased by a factor of ca. 2.

Pyridine too accelerated the decarboxylation rate of  $3^{+\bullet}$  and  $4^{+\bullet}$ . Very interestingly, in both cases the plot of the observed rate constants against pyridine concentrations was not linear but reached a plateau at higher concentrations of pyridine as shown in Figure 4. The  $k_{\text{obs}}$  value at the plateau was almost the same (ca.  $2 \times 10^7 \text{ s}^{-1}$ ) for  $3^{+\bullet}$  and  $4^{+\bullet}$ . The same phenomenon was observed with 4-cyanopyridine, but the rate constant corresponding to the plateau was lower than with pyridine (ca.  $4 \times 10^6 \text{ s}^{-1}$ , Figure S1, Supporting Information).

Laser photolysis experiments were also carried out with the tetramethylammonium salts  $\text{PhSCH}_2\text{CO}_2\text{NMe}_4$  and  $\text{PhSCH(Ph)CO}_2\text{NMe}_4$  formed from **3** and **4**, respectively. The sensitizer was 1,4-dicyanonaphthalene (DCN) since with  $\text{NMQ}^+$  there were problems in the laser photolysis experiments, probably due to some interaction between the cationic sensitizer and the carboxylate. In these experiments, however, no transient attributable to a zwitterionic radical cation was observed. Only signals corresponding to the carbon radical were detected together with those of  $\text{DCN}^{\bullet-}$  ( $\lambda_{\text{max}} = 390$  nm)<sup>9</sup> and the triplet state of DCN (400–500 nm)<sup>9</sup> (Figure S2, Supporting Information). Probably, the decarboxylation of the zwitterionic radical

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**FIGURE 4.** Observed rate constant for the decay of  $3^{+\bullet}$  (a) and  $4^{+\bullet}$  (b) vs pyridine concentration in  $\text{CH}_3\text{CN}$ .

cation occurs immediately after the laser pulse as also observed by Filipiak et al.<sup>1a</sup>

**Steady-State Experiments.** Photooxidation reactions were carried out in a photoreactor equipped with 10 lamps (360 nm; 14 W each) and thermostated at 25 °C. The substrate concentration was  $1 \times 10^{-2}$  M and that of the sensitizer  $1 \times 10^{-3}$  M in Ar-saturated  $\text{CH}_3\text{CN}$ . Generally, the sensitizer was  $\text{NMQ}^+$ , as in the laser photolysis experiments. However, 2,4,6-triphenylpyrylium tetrafluoroborate (TPP), 1,2,4,5-tetracyanobenzene (TCB), and 1,4-dicyanonaphthalene (DCN) were also used for reasons which will be discussed below. Since the kinetic investigation had shown that the decay of all radical cations is accelerated by the presence of  $\text{H}_2\text{O}$ , most photolyses were performed in  $\text{CH}_3\text{CN}$  containing 5% of  $\text{H}_2\text{O}$  in order to have more efficient and reproducible reactions. The reaction time was 30 min in all cases. All results are collected in Table 2.

The silyl derivative **1** and the carboxylic acid **3** exhibited very similar behaviors. With  $\text{NMQ}^+$  as the sensitizer and in  $\text{CH}_3\text{CN}$ –5%  $\text{H}_2\text{O}$ , both compounds produced thioanisole as the only reaction product in a process which did not consume the sensitizer (Scheme 3). The same outcome was observed when the photolysis of **1** was sensitized by TPP or TCB. When **1** and **3** were photolyzed in  $\text{CH}_3\text{CN}$ –5%  $\text{D}_2\text{O}$  a selective incorporation of a single deuterium atom into the methyl group of thioanisole was observed. However, no incorporation of deuterium in the product was observed when the photolysis of **1** was carried out in  $\text{CD}_3\text{CN}$ .

A completely different situation was found with **2** and **4**. In this case, with  $\text{NMQ}^+$ , both substrates produced 1,2-bis-(phenylsulfanyl)-1,2-diphenylethane (a *meso/d,l* mixture) (**5**) as the only product (Scheme 3).

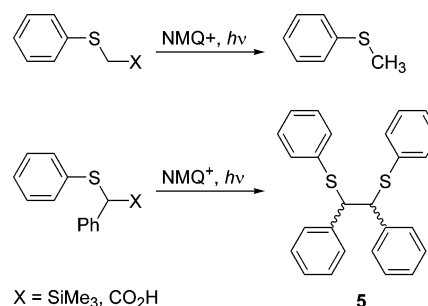
These reactions were much less efficient than those of **1** and **3**, simply because in this case the sensitizer is consumed and only 10% of sensitizer with respect to the substrate was used.<sup>10</sup> On the other hand, if the reaction time is lengthened or more catalyst is used some photolysis of **5** also occurred, which complicated the product analysis. The same results were

**TABLE 2.** Steady-State Photosensitized Oxidations of **1–4** in Deaerated  $\text{CH}_3\text{CN}$ <sup>a</sup>

sensitizer	additives <sup>b</sup>	products (yield, %) <sup>c</sup>
PhSCH <sub>2</sub> SiMe <sub>3</sub> ( <b>1</b> )		
NMQ <sup>+</sup>		PhSCH <sub>3</sub> (27)
	H <sub>2</sub> O	PhSCH <sub>3</sub> (72)
	D <sub>2</sub> O	PhSCH <sub>2</sub> D (70)
TPP		PhSCH <sub>3</sub> (38)
TCB		PhSCH <sub>3</sub> (11)
DCN	H <sub>2</sub> O	PhSCH <sub>3</sub> (41)
PhSCH <sub>2</sub> CO <sub>2</sub> H ( <b>3</b> )		
NMQ <sup>+</sup>	H <sub>2</sub> O	PhSCH <sub>3</sub> (16)
	pyridine	PhSCH <sub>3</sub> (55)
TCB	H <sub>2</sub> O	PhSCH <sub>3</sub> (6.0)
PhSCH(Ph)SiMe <sub>3</sub> ( <b>2</b> )		
NMQ <sup>+</sup>	H <sub>2</sub> O	[PhSC(Ph)H] <sub>2</sub> ( <b>6</b> )
TPP		[PhSC(Ph)H] <sub>2</sub> ( <b>5</b> )
TCB		[PhSC(Ph)H] <sub>2</sub> ( <b>2</b> ) <sup>d</sup>
DCN	H <sub>2</sub> O	PhSCH <sub>2</sub> Ph (92)
PhSCH(Ph)CO <sub>2</sub> H ( <b>4</b> )		
NMQ <sup>+</sup>	H <sub>2</sub> O	[PhSC(Ph)H] <sub>2</sub> ( <b>5</b> )
	pyridine	[PhSC(Ph)H] <sub>2</sub> ( <b>4</b> )

<sup>a</sup> General conditions: substrate  $10^{-2}$  M, sensitizer  $10^{-3}$  M,  $T = 25$  °C, irradiation time = 30 min. <sup>b</sup> When present,  $\text{H}_2\text{O} = 5\%$  v/v, pyridine  $2 \times 10^{-2}$  M,  $\text{D}_2\text{O} = 5\%$  v/v. <sup>c</sup> Referred vs the substrate. Determined by GC or <sup>1</sup>H NMR in the case of **5**. <sup>d</sup> Adducts of the PhSC•H(Ph) radical with the sensitizer were also detected.

### SCHEME 3



obtained with TPP and TCB as the sensitizers. However, with DCN, **2** afforded a high yield of benzyl phenyl sulfide and no consume of sensitizer was observed. All results are collected in Table 2.

### Discussion

**Kinetic Results.** The laser photolysis experiments together with the steady state ones have clearly shown that the photolysis of **1–4** sensitized by  $\text{NMQ}^+$  leads to the formation of the corresponding radical cations and that these species decay, forming an  $\alpha$ -thiophenyl carbon radical (Scheme 4).

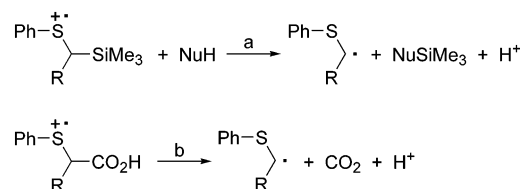
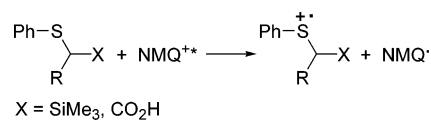
The C–Si bond cleavage in  $1^{+\bullet}$  and  $2^{+\bullet}$  (reaction a in Scheme 4) is nucleophilically assisted. In the absence of added nucleophiles, the assistance to C–Si bond cleavage can be provided by the solvent itself or more probably by the residual water present in  $\text{CH}_3\text{CN}$ . A quantitative assessment of such a nucleophilic assistance was determined for MeOH (Table 1), and it is of interest to compare the second-order rate constant for the MeOH-assisted fragmentation of  $1^{+\bullet}$  ( $3.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) with the value of  $7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  found for the MeOH-assisted desilylation of the radical cation of PhN(Me)CH<sub>2</sub>SiMe<sub>3</sub> (**6**) in  $\text{CH}_3\text{CN}$ .<sup>11</sup> Since  $6^{+\bullet}$  is much more stable than  $1^{+\bullet}$ ,<sup>12</sup>

(10) No effort was made to determine the fate of the quinoline radical that probably undergoes a dimerization process.

(11) Su, Z.; Mariano, P. S.; Falvey, D. E.; Yoon, U. C.; Oh, S. W. *J. Am. Chem. Soc.* **1998**, *120*, 10676.



## SCHEME 4

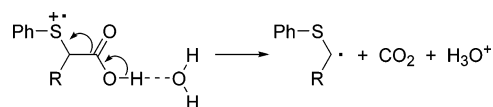


whereas the formed carbon radicals have very close stability,<sup>13</sup> the observation of a similar desilylation rate is noteworthy. Accordingly a much slower desilylation of  $6^{+\bullet}$  would have been expected on purely thermodynamic grounds. An intrinsic larger reactivity of a nitrogen radical cation with respect to that of a structurally similar sulfur radical cation was already observed by comparing the C–C bond cleavage reactions of  $\beta$ -amino alcohol and  $\beta$ -sulfide alcohol radical cations.<sup>1c</sup> The phenomenon was attributed to a more favorable orbital overlap between the SOMO on the heteroatom and the  $\sigma$  orbital of the scissile bond in the former than in the second radical cation. Thus, in a nitrogen radical cation, the intrinsic barrier for the intramolecular electron transfer leading to the cleavage should be lower than in a sulfur radical cation. It is reasonable to suggest that this explanation also holds for the C–Si bond cleavage reaction.

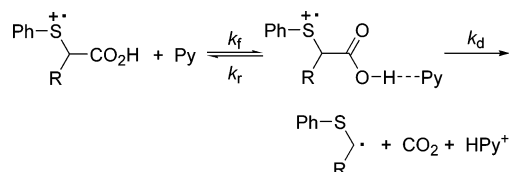
Of some interest is also the comparison between the MeOH-assisted decay rate of  $1^{+\bullet}$  and that ( $5.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) of the radical cation of 4-methoxybenzyltrimethylsilane (MBTM $^{+\bullet}$ ).<sup>14</sup> The rate constants are very similar, although the reduction potential of  $1^{+\bullet}$  is significantly lower than that of MBTM (1.35 V vs SCE)<sup>2d</sup> and the benzyl radical is significantly more stable than PhSCH $_2^{\bullet}$ .<sup>15</sup> Thus, again on thermodynamic grounds, we would expect a larger rate for MBTM $^{+\bullet}$ . A plausible explanation is that in  $1^{+\bullet}$  the positive charge, mostly located on sulfur, is very close to the C–Si bond, whereas in MBTM $^{+\bullet}$  it is largely localized in the aromatic ring where it is stabilized by the methoxy group. Therefore, the intrinsic barrier for intramolecular electron transfer should be smaller with  $1^{+\bullet}$  than with MBTM $^{+\bullet}$ .

An additional observation concerning the reactivity of silyl derivatives (Table 1) is that the desilylation rate is ca. 30 times faster for  $2^{+\bullet}$  than for  $1^{+\bullet}$ . This difference may be reasonably attributed to the much higher stability of the more delocalized phenyl substituted carbon radical formed in the former case. However, it has been recently suggested that in fragmentation reactions of radical cation the possibility of delocalization of spin or charge in one of the fragments may be an unfavorable factor since it should increase the intrinsic barrier of the

## SCHEME 5



## SCHEME 6



process.<sup>2b</sup> Evidently, in the reaction of silyl derivatives such a kinetic factor is insufficient to overcome the very large driving force for the formation of the phenyl-substituted carbon radical.

Passing to discuss the reactivity data of the carboxylic acids, it can be first noted that the difference in reactivity between  $3^{+\bullet}$  and  $4^{+\bullet}$  (ca. 3 times) is much smaller than that between  $1^{+\bullet}$  and  $2^{+\bullet}$ . It seems therefore that in this case the stability of the formed carbon radical has little influence on the fragmentation rate of the carbon radical. It is also noteworthy that with both  $3^{+\bullet}$  and  $4^{+\bullet}$ , the decay rate constants are significantly increased by addition of H $_2$ O. With 5% H $_2$ O, there is an increase in rate of at least an order of magnitude. A possible suggestion is that in the radical cation C–C bond cleavage is concerted with CO $_2$ H deprotonation. Thus, as shown in Scheme 5, the favorable effect of H $_2$ O might be due to its capacity of assisting O–H bond breaking by hydrogen bond formation.

A mechanism where C–C bond cleavage is concerted with O–H proton transfer also accounts for the deuterium kinetic isotope effect ( $k_H/k_D = 2$ ) which was observed when the reaction was carried out in the presence of D $_2$ O, which indicates that the transfer of the proton is part of the reaction coordinate.

Pyridines too had a favorable effect on the decay rate of  $3^{+\bullet}$  and  $4^{+\bullet}$  but exhibited the peculiar behavior shown in Figure 4. Such behavior is typical of a reaction which involves first the reversible and fast formation of an intermediate between the radical cation and the base that then decomposes to products.<sup>16</sup> In this case, the intermediate might reasonably be a H-bonded complex between the radical cation and pyridine since the possibility that it is the radical zwitterion formed by deprotonation of the radical cation can be excluded since the rate constants corresponding to the plateau are different for pyridine and 4-cyanopyridine.<sup>17</sup> Thus, the reaction mechanism may be that depicted in Scheme 6.

When the reverse reaction rate of the H-bonded complex to reactants,  $k_r$ , is much faster than its fragmentation rate,  $k_d$ , eq 1 holds, where  $K$  is the formation constant of the complex and [Py] is the initial concentration of pyridine (in strong excess with respect to that of the radical cation).<sup>16,18</sup>

$$1/k_{\text{obs}} = 1/k_d + 1/k_d K [\text{Py}] \quad (1)$$

Thus, a plot of  $1/k_{\text{obs}}$  vs  $1/[\text{Py}]$  should give a linear trend observed with both  $3^{+\bullet}$  and  $4^{+\bullet}$  (Figures 5 and S1, Supporting Information).

(12) (a) The oxidation potential of **6** should be significantly lower than that of *N,N*-dimethylaniline (0.77 V vs SCE)<sup>12b</sup> and, hence, much lower than that of **1** that is 1.15 V vs SCE.<sup>1k</sup> (b) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1991**, *113*, 8778.

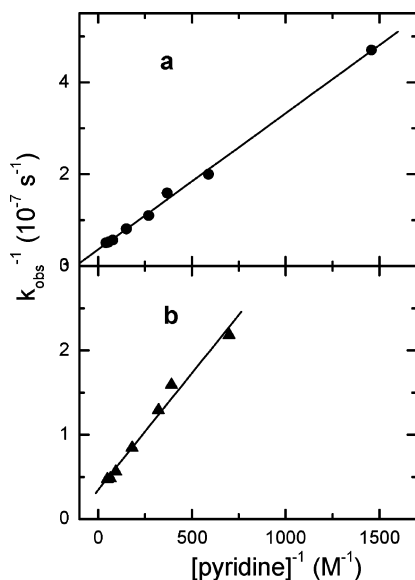
(13) (a) This is indicated by the similar bond energies of PhSCH $_2$ –H and PhN(CH $_3$ )CH $_2$ –H, 93<sup>13b</sup> and 91.7 kcal/mol,<sup>13c</sup> respectively. (b) Zhang, X. M.; Bordwell, F. G.; Van Der Puy, M.; Fried, H. E. *J. Org. Chem.* **1993**, *58*, 3060. (c) Dombrowski, G. W.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Org. Chem.* **1999**, *64*, 427.

(14) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Mattes, S. L.; Todd, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8973.

(15) (a) This is indicated by the different bond energies of PhSCH $_2$ –H and PhSCH(Ph)–H, 93<sup>13b</sup> and 82.2 kcal/mol,<sup>15b</sup> respectively. (b) Measured in DMSO. Bordwell, F. G.; Liu, W.-Z. *J. Phys. Org. Chem.* **1998**, *11*, 397.

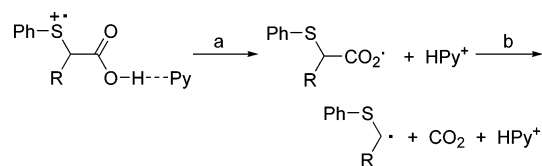
(16) Cox, B. G. *Modern Liquid-Phase Kinetics*; Compton, R. G., Davies, S. G., Evans, J., Eds.; Oxford University Press: Oxford, U.K., 1994; pp 31–32.

(17) Moreover, in the laser photolysis experiments carried out with the carboxylate anions it was not possible to observe the radical cation as it decays immediately after the laser pulse.



**FIGURE 5.**  $1/k_{\text{obs}}$  vs  $1/[\text{pyridine}]$  for the decay of  $3^{+\bullet}$  (a) and  $4^{+\bullet}$  (b) in  $\text{CH}_3\text{CN}$ .

#### SCHEME 7



The reciprocal of the line intercept provides,  $k_d$  values of  $2.8 \times 10^7 \text{ s}^{-1}$  and  $2.2 \times 10^7 \text{ s}^{-1}$  for the H-bonded complex from  $3^{+\bullet}$  and  $4^{+\bullet}$ , respectively, that are very close to the values of  $k_{\text{obs}}$  corresponding to the plateau in Figure 4. With  $3^{+\bullet}$  and 4-cyanopyridine (Figure S1, Supporting Information),  $k_d$  is  $4.3 \times 10^6 \text{ s}^{-1}$ , which compares with the value of  $4 \times 10^6 \text{ s}^{-1}$  for the  $k_{\text{obs}}$  corresponding to the plateau in Figure S1 (Supporting Information).

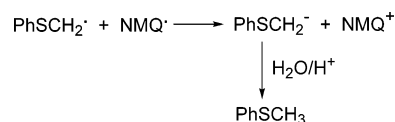
The observation of similar values of  $k_d$  for  $3^{+\bullet}$  and  $4^{+\bullet}$  is very remarkable since it indicates that there is no influence of the stability of the formed radical upon the fragmentation rate of the H-bonded complex. This suggests that the fragmentation may occur in two steps. In the first step, the hydrogen-bonded radical cation undergoes a proton-coupled intramolecular electron transfer leading to a carboxyl radical (Scheme 7, path a). In the second step, the carboxyl radical loses  $\text{CO}_2$  and produces the carbon radical (Scheme 7, path b).

If the first step is rate determining, no effect of the stability of the formed radical upon the fragmentation rate of the complex is expected. That an electron-transfer process be coupled to proton transfer is a mechanistic possibility that has received great attention and support in recent times.<sup>19</sup> Thus, the suggestion that also an intramolecular electron transfer can be coupled to a proton transfer as in path a of Scheme 7 seems reasonable. A final notation is that, with  $3^{+\bullet}$ , the difference in  $k_d$  between

(18) The treatment neglects the decay rate of the radical cation in the absence of pyridine. This approximation is justified as this rate is significantly less than that of the H-bonded complex and the constant for the formation of the complex should be quite large. From the slope and intercept of the plots in Figure 5, values of 124 and 125  $\text{M}^{-1}$  are obtained for  $3^{+\bullet}$  and  $4^{+\bullet}$ , respectively.

(19) Shukla, D.; Young, R. H.; Farid, S. J. *Phys. Chem. A* **2004**, *108*, 10386 and references therein.

#### SCHEME 8



pyridine ( $\text{p}K_a = 12.3$  in  $\text{CH}_3\text{CN}$ )<sup>20</sup> and 4-cyanopyridine ( $\text{p}K_a = 8.0$  in  $\text{CH}_3\text{CN}$ ),<sup>20</sup>  $2.8 \times 10^7 \text{ s}^{-1}$  vs  $4.3 \times 10^6 \text{ s}^{-1}$ , is rather small, indicating that step a in Scheme 7 is almost insensitive ( $\beta \sim 0.19$ ) to the strength of the base.

**Product Formation.** There is no doubt that, for all substrates, the products observed in the steady-state photolyses derive from the carbon radicals formed in the fragmentation reactions described in Scheme 4. The results reported in Table 2 clearly indicate that both for the acids and the silanes the fate of the carbon radical appears to depend on the nature of the group R. Accordingly, when  $\text{R} = \text{H}$  (compounds **1** and **3**), the carbon radical is  $\text{PhSCH}_2^\bullet$  and the exclusive reaction product is thioanisole, while, when  $\text{R} = \text{Ph}$  (compounds **2** and **4**), the product is the 1,2-bis(phenylsulfanyl)-1,2-diphenylethane (**5**), that is the dimer of the carbon radical  $\text{PhSC}^\bullet\text{H(Ph)}$  (Scheme 3).

In the reactions leading to thioanisole the sensitizer acted as a catalyst and significant yields of product were obtained. In the reactions leading to **5**, the sensitizer was consumed and the yield of product (corresponding to the initial amount of sensitizer) was much lower.

Further investigation of the reaction leading to thioanisole was deemed necessary, as it represents an interesting case of a *nonoxidative* desilylation with **1** and a *nonoxidative* decarboxylation with **3**, obtained under oxidizing conditions. Thus, to determine the origin of hydrogen which converts  $\text{PhSCH}_2^\bullet$  into  $\text{PhSCH}_3$ , experiments were carried out in  $\text{CD}_3\text{CN}$  and in  $\text{CH}_3\text{CN}$  in the presence of  $\text{D}_2\text{O}$ . No incorporation of D into thioanisole was observed in the former whereas, when the photolyses of **1** and **3** were run in  $\text{CH}_3\text{CN}$  with 5% of  $\text{D}_2\text{O}$ ,  $\text{PhSCH}_2\text{D}$  was the reaction product. These experiments exclude a free radical hydrogen abstraction for the conversion of  $\text{PhSCH}_2^\bullet$  into  $\text{PhSCH}_3$  and suggest instead an ionic process.

A reasonable hypothesis might be that  $\text{PhSCH}_2^\bullet$  is reduced by  $\text{NMQ}^\bullet$ , with regeneration of  $\text{NMQ}^+$ . A carbanion is formed that reacts with  $\text{H}_2\text{O}/\text{H}^+$  to produce thioanisole (Scheme 8). This hypothesis, however, seems unlikely on the following grounds.

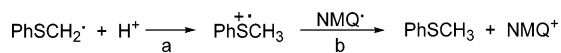
First, the reduction potential of  $\text{PhSCH}_2^\bullet$  that can be estimated to be around  $-1.13 \text{ V}$  vs SCE<sup>21</sup> is more negative than that of  $\text{NMQ}^+$  ( $-0.85 \text{ V}$  vs SCE).<sup>22</sup> Thus, the reduction of  $\text{PhSCH}_2^\bullet$  by  $\text{NMQ}^\bullet$  is endergonic. Second,  $\text{PhSC}^\bullet\text{H(Ph)}$  is expected to be more easily reducible than  $\text{PhSCH}_2^\bullet$ , as its reduction potential ( $-0.926 \text{ V}$  vs SCE)<sup>15b</sup> is less negative than that of  $\text{PhSCH}_2^\bullet$  and it is therefore difficult to explain why this radical is not reduced under the same reaction conditions. Third and more significantly, conversion of **1** and **3** into  $\text{PhSCH}_3$  was also obtained when photosensitizers with much less negative reduction potential than  $\text{NMQ}^+$  like TCB ( $E_{\text{red}} = -0.66 \text{ V}$  vs SCE)<sup>23</sup>

(20) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 6, 7472.

(21) (a) Value estimated in DMSO using the Bordwell equation ( $\text{BDE} = 1.37\text{p}K_a + E_{\text{red}}(\text{radical, vs NHE})23.1 + 56$ )<sup>21b</sup> where  $\text{BDE}$  of  $\text{PhSCH}_2\text{H}$  is 93 kcal/mol,<sup>13b</sup> and the  $\text{p}K_a$  of  $\text{PhSCH}_3$  in DMSO is 42.<sup>21c</sup> (b) Bordwell, F. G.; Cheng, J.; Ji, G. Z.; Satish, A. V.; Zhang, X. *J. Am. Chem. Soc.* **1991**, *113*, 9790. (c) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(22) Yoon, U. C.; Quillen, S. L.; Mariano, P. S.; Swanson, R.; Stavinocha, J. L.; Bay, E. *J. Am. Chem. Soc.* **1983**, *105*, 1204–1218.

## SCHEME 9



and even TPP (−0.24 vs SCE)<sup>24</sup> were used. On the other hand, when **2** was photolyzed using a sensitizer, DCN, with a reduction potential of −1.26V vs SCE,<sup>25</sup> more negative of that of PhSC•H(Ph), the reduction product PhSCH<sub>2</sub>Ph was obtained in high yield (no consume of the sensitizer). Clearly, Scheme 8, with DCN in the place of NMQ<sup>+</sup>, holds in this case.

An alternative hypothesis to account for the non-oxidative desilylation is that the carbon radical is protonated to form a radical cation which then is reduced by NMQ<sup>+</sup> with regeneration of NMQ<sup>+</sup> (Scheme 9).

The proton for reaction a in Scheme 9 may be provided by the acid formed in the fragmentation reaction of the radical cation (Scheme 4, paths a and b) and accordingly no thioanisole was formed when the photolysis of **1** sensitized by TCB was performed in the presence of a small amount of Na<sub>2</sub>CO<sub>3</sub>.<sup>26</sup> Other products were observed, mostly diphenyl disulfide and thiophenol, probably coming from further photolysis of addition products between PhSCH<sub>2</sub>• and the sensitizer and/or its radical anion.

In the framework of the mechanism in Scheme 9, the drastically different behaviors of PhSCH<sub>2</sub>• and PhSC•H(Ph) may be justified by the great difference in their pK<sub>a</sub>. Accordingly, it can be calculated that in CH<sub>3</sub>CN the pK<sub>a</sub> of (PhSCH<sub>3</sub>)<sup>+</sup> is 3.6<sup>27</sup> whereas that of (PhSCH<sub>2</sub>Ph)<sup>+</sup> is −5.6.<sup>28</sup> Thus, the protonation of PhSCH<sub>2</sub>• may occur several orders of magnitude faster than that of PhSC•H(Ph) so that only with the former radical it can overcome the competitive dimerization reaction. In this respect, it is noteworthy that pulse radiolysis experiments have shown that the deprotonation of (PhSCH<sub>3</sub>)<sup>+</sup> in H<sub>2</sub>O is too slow to be measured (*k* < 30 s<sup>−1</sup>). In contrast, the deprotonation rate of (PhSCH<sub>2</sub>Ph)<sup>+</sup> is 2.5 × 10<sup>3</sup> s<sup>−1</sup>.<sup>10</sup>

With respect to the above hypothesis, it can also be noted that very recently Hanzlik and his associates suggested the protonation of the carbon radical Ph(Me)NCH<sub>2</sub>• to explain the formation of *N,N*-dimethylaniline in the H<sub>2</sub>O<sub>2</sub>-induced oxidation of *N*-methyl-*N*-phenylglycine catalyzed by horseradish peroxidase (HRP).<sup>29</sup> Our own observation that also the reaction of **3** with H<sub>2</sub>O<sub>2</sub>/HRP produces thioanisole<sup>30</sup> shows that the process may be general and to some extent lends support to the mechanism proposed in Scheme 9.

## Conclusions

Laser and steady-state photolysis in CH<sub>3</sub>CN of the silyl sulfides **1** and **2** and the phenylthioacetic acids **3** and **4**, mostly

with NMQ<sup>+</sup> as the sensitizer, lead to the corresponding radical cations that undergo a fragmentation reaction involving C–Si bond cleavage (**1**<sup>+</sup> and **2**<sup>+</sup>) and C–C bond cleavage (**3**<sup>+</sup> and **4**<sup>+</sup>). An α-thiophenyl carbon radical is produced, namely PhSCH<sub>2</sub>• from **1**<sup>+</sup> and **3**<sup>+</sup> and PhSC•H(Ph) from **2**<sup>+</sup> and **4**<sup>+</sup>. The products study showed that the two radicals undergo a different fate: PhSCH<sub>2</sub>• is converted into PhSCH<sub>3</sub> whereas PhSC•H(Ph) dimerizes to [PhSC(Ph)H]<sub>2</sub>. Evidence is presented suggesting that PhSCH<sub>3</sub> is formed by protonation of PhSCH<sub>2</sub>•. A radical cation is produced that is then reduced to PhSCH<sub>3</sub> by NMQ<sup>+</sup>. Protonation of PhSC•H(Ph) may be much slower since the basicity of this radical (pK<sub>a</sub> = −5.6) is much lower than that of PhSCH<sub>2</sub>• (pK<sub>a</sub> = 3.6). Thus, the preferred reaction of PhSC•H(Ph) is the dimerization.

The kinetic study of the fragmentation reactions allowed a number of conclusions. The rate of C–Si bond cleavage is very sensitive to the stability of the formed carbon radical as **2**<sup>+</sup> resulted 30 times more reactive than **1**<sup>+</sup>. This contrasts with the decarboxylation reaction where **4**<sup>+</sup> was only 3–6 times more reactive than **3**<sup>+</sup>, depending on the reaction conditions. The rates of the decarboxylation reactions are significantly accelerated by the presence of water, and the phenomenon suggests that the C–C bond scission in the radical cation is concerted with H<sub>2</sub>O-assisted CO<sub>2</sub>H deprotonation. Pyridine too increases the fragmentation rates of **3**<sup>+</sup> and **4**<sup>+</sup>; the increase, however, is not a linear function of base concentration, but a plateau is reached at higher base concentrations. This result is interpreted on the basis of a mechanism involving the fast and reversible formation of a H-bonded complex between the radical cation and the base. The following fragmentation of the H-bonded complex probably occurs in two steps. In the first step (that is rate determining), a proton-coupled intramolecular electron transfer takes place leading to a carboxyl radical. Fast loss of CO<sub>2</sub> from the carboxyl radical occurs in the second step.

## Experimental Section

**Materials.** (Phenylsulfanylmethyl)trimethylsilane (**1**) and phenylsulfanylacetic (**3**) acid were purchased and used as received. Phenyl(phenylsulfanyl)acetic acid (**4**),<sup>31</sup> [phenyl(phenylsulfanyl)methyl]trimethylsilane (**2**),<sup>32</sup> 1,2-bis(phenylsulfanyl)-1,2-diphenylethane (a 1:1 *meso/d,l* mixture) (**5**),<sup>33</sup> and *N*-methylquinolinium tetrafluoroborate<sup>34</sup> were prepared according to literature procedures. Tetramethylammonium salts of **3** and **4** were prepared by reacting the corresponding acids with an equimolecular amount of tetramethylammonium hydroxide in methanol and recrystallized from dichloromethane/hexane. Thioanisole, 1,4-dicyanonaphthalene, 1,2,4,5-tetracyanobenzene, 2,4,6-triphenylpyrylium tetrafluoroborate, pyridine, 4-cyanopyridine, acetonitrile (HPLC plus grade), and toluene were purchased and used as received.

**Laser Flash Photolysis.** Excitation wavelengths of 308 nm (from a XeCl excimer laser, pulse width ca. 15 ns and energy <3 mJ per pulse) and 355 nm (from a Nd:YAG laser, Continuum, third harmonic, pulse width ca. 7 ns and energy <3 mJ per pulse) were used in nanosecond flash photolysis experiments.<sup>35</sup>

The transient spectra were obtained by a point-to-point technique, monitoring the change of absorbance (ΔA) after the laser flash at

(23) Mella, M.; Freccero, M.; Albini, A. *Chem. Commun.* **1995**, 41.

(24) Doménech, A.; García, H.; Alvaro, M.; Carbonell, E. *J. Phys. Chem. B* **2003**, *107*, 3040.

(25) Huang, Y.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1994**, *116*, 2157.

(26) In this experiment, TCB was the sensitizer since with NMQ<sup>+</sup> it seems that there is some reaction of the cationic sensitizer with the basic medium and the reaction was less efficient, anyway no thioanisole was observed also in this case.

(27) (a) Calculated on the basis of a thermochemical cycle by the equation pK<sub>a</sub> = 1/1.37[ΔG°(PhSCH<sub>2</sub>–H) + 23.06E°(H•/H<sup>+</sup>) – 23.06E°(PhSCH<sub>3</sub>)] where ΔG°(PhSCH<sub>2</sub>–H) is given by the BDE of the bond (93 kcal/mol)<sup>13b</sup> minus the entropic contribution taken as 8 kcal/mol at 298 K, E°(H•/H<sup>+</sup>) is −2.00 V vs SCE in CH<sub>3</sub>CN<sup>27b</sup> and E°(PhSCH<sub>3</sub>) is 1.47 V vs SCE.<sup>1k</sup> (b) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287.

(28) As in ref 25 with BDE(PhSCPh–H) = 82.2 kcal/mol<sup>15b</sup> and E°(PhSCH<sub>2</sub>Ph) = 1.55V vs SCE.<sup>1k</sup>

(29) Totah, R. A.; Hanzlik, R. P. *J. Am. Chem. Soc.* **2002**, *124*, 10000.

(30) Baciocchi, E.; Gerini, M. F. To be published.

(31) Lehto, S.; Shirley, D. A. *J. Org. Chem.* **1957**, *22*, 989.

(32) Ager, D. J. *J. Chem. Soc., Perkin Trans. 1* **1986**, 195

(33) (a) Alnajjar, M. S.; Franz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 1052.

(b) Kauffman, T. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 291–304.

(34) Donovan, P. F.; Conley, D. A. *J. Chem. Eng. Data* **1966**, *11*, 614.

(35) (a) Romani, A.; Elisei, F.; Masetti, F.; Favaro, G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2147. (b) Görner, H.; Elisei, F.; Aloisi, G. G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 29.

intervals of 5–10 nm over the spectral range 300–800 nm, averaging at least 10 decays at each wavelength. The lifetime values (the time at which the initial signal is reduced to  $1/e$ , experimental error of  $\pm 10\%$ ) are reported for transients showing first-order decay kinetics. Nitrogen or oxygen was bubbling through the solution. All measurements were carried out at  $22 \pm 2$  °C unless otherwise indicated.

**Steady-State Photooxidation General Procedure.** Photooxidation reactions were carried out in a photoreactor equipped with 10 lamps (360 nm; 14 W each). A 4 mL solution containing the substrate ( $1 \times 10^{-2}$  M) and the photosensitizer ( $1 \times 10^{-3}$  M) in Ar-saturated  $\text{CH}_3\text{CN}$  and, when present,  $\text{H}_2\text{O}$  (5% v/v) was irradiated in a rubber cap-sealed jacketed tube for 30 min, thermostated at 25 °C by a Peltier apparatus. In some cases, pyridine ( $2 \times 10^{-2}$  M) was present. An internal standard (4-methylbenzophenone) was added, and the mixture was analyzed by GC, GC–MS, and  $^1\text{H}$  NMR. In photooxidation reactions carried out in the presence of  $\text{Na}_2\text{CO}_3$ , the procedure is identical as reported above except for the presence of 30 mg of the salt and for the solution stirring during the irradiation. Blank experiments, carried out by irradiating the solution in the absence of the sensitizer, did not show in all cases product formation.

**Determination of Deuterium Incorporation.** The procedure was identical as reported above.  $\text{D}_2\text{O}$  (5% v/v, 99.9% *d*) was present in the reaction medium. Deuterium incorporation was determined by GC–MS analysis of thioanisole by the ratio of the intensity of the molecular peaks  $m/z = 124$  and 125, corrected for the  $^{13}\text{C}$  contribution.

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**Supporting Information Available:** Preparation and characterization of **2** and **4**. Table of absorption maxima and transients produced by LFP in  $\text{N}_2$ -saturated  $\text{CH}_3\text{CN}$ . Plots of  $k_{\text{obs}}$  vs [4-CN-pyridine] and  $1/k_{\text{obs}}$  vs  $1/[4\text{-CN-pyridine}]$  for the decay of  $3^{+\bullet}$ . Time-resolved absorption spectra of the 1,4-dicyanonaphthalene/PhSCH-(Ph)CO<sub>2</sub>NMe<sub>4</sub> system in  $\text{N}_2$ -saturated  $\text{CH}_3\text{CN}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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