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Nature of the Chain Propagation in the Photostimulated Reaction of 1-Bromonaphthalene with Sulfur-Centered Nucleophiles

Luciana C. Schmidt, Juan E. Argüello,* and Alicia B. Peñéñory*

INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina

penenory@fcq.unc.edu.ar; jea@fcq.unc.edu.ar

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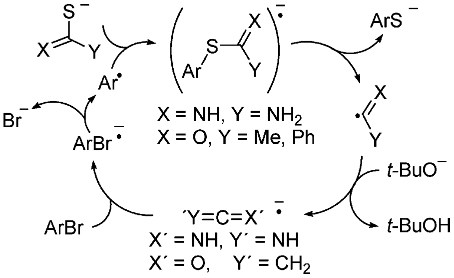

The reactivity of $^{-}SC(NH)NH_2$ (**1**), $MeCOS^-$ (**2**), and $PhCOS^-$ (**3**) toward 1-naphthyl radicals was studied in DMSO. The photostimulated reaction of anions **1**, **2**, and **3** with 1-bromonaphthalene (**4**) after quenching with MeI renders 1-(methylthio)naphthalene (**6**) as a main product together with bis(1-naphthyl) sulfide (**7**) and naphthalene (**5**). The thioacetate ion (**2**) and thiobenzoate ion (**3**) were unreactive toward **4** as electron-donor under photostimulation; however, in the presence of potassium *tert*-butoxide anion (entrainment conditions), they gave the mentioned products **5**, **6**, and **7**, after the addition of MeI. Quenching of the triplet state of **4** was assigned as the photoinduced initiation step, with a rate constant value of $(4.6 \pm 0.5) \times 10^8$ M^{-1} s^{-1} for *tert*-butoxide anion and a rough estimated value of $(8 \pm 7) \times 10^7$ M^{-1} s^{-1} for anion **1**. By using hydrogen abstraction from DMSO as the competitive reaction, the absolute rate constants for the addition of anions **1**, **2**, and **3** to 1-naphthyl radicals have been determined to be 1.0×10^9, 1.2×10^9, and 3.5×10^9 M^{-1} s^{-1}, respectively. This reactivity order is in agreement with the stability of the resulting radical anions $(ArNu)^{\bullet-}$ $(\mathbf{10}-\mathbf{12})^{\bullet-}$. The inhibition experiments of the photoinduced substitution reaction in the presence of radical scavengers and the global quantum yield higher than the unity are evidence of a radical chain mechanism for these substitution reactions by anions **1** and **2**. Anion **3** adds to the 1-naphthyl radical, but is neither able to initiate nor to keep the propagation cycle. Evaluation of the electron-transfer driving forces for the reaction between $(ArNu)^{\bullet-}$ and **4** together with the absence of a chain reaction for the anion **3** indicate that the propagation in the proposed mechanism is given by an acid−base reaction between the radical $^{\bullet}C(O)Me$ or $^{\bullet}C(NH)NH_2$ (**13**) and a base.

Introduction

Radical nucleophilic substitution involving electron-transfer (ET) steps or $S_{RN}1$ mechanism has proven to be a versatile mechanism for replacing an adequate leaving group at the ipso position by a nucleophile. This process has a considerably broad scope in relation to substrates and nucleophiles, and the most relevant results as well as synthetic applications have been widely reviewed.[1] The mechanism of this reaction is a chain process with radicals and radical anions as intermediates, whose initiation step involves an ET to the substrate. The general accepted pathways for the propagation cycle are outlined in Scheme 1.

Although the most extensively used initiation method is a photoinduced ET (PET) from a charged nucleophile to the substrate, there are not many studies on its mechanism. These PETs can be accomplished in one of the following pathways: (1) photoexcitation of a charge-transfer complex (CTC) formed

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* Corresponding authors. Phone: (+54) 351-4334170/73. Fax: (+54) 351-4333030/4334174.

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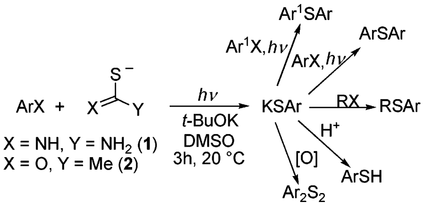
SCHEME 1

$$(RX)^{-\bullet} \longrightarrow R^{\bullet} + X^{-} \qquad (1)$$

$$R^{\bullet} + Nu^{-} \longrightarrow (RNu)^{-\bullet} \qquad (2)$$

$$(RNu)^{-\bullet} + RX \longrightarrow RNu + (RX)^{-\bullet} \qquad (3)$$

SCHEME 2



between the nucleophile and the substrate followed by ET;[2−6] (2) homolytic cleavage of the C−X bond;[3] (3) ET from an excited nucleophile to the substrate;[7,8] (4) ET from a nucleophile to an excited substrate;[9] and (5) photoejection of an electron from an excited nucleophile.[10]

For nucleophiles that are unreactive at initiation but quite reactive at propagation, the addition of minute amounts of another nucleophile able to initiate the reaction increases the generation of intermediates. This allows the less reactive initiation-nucleophile to start its own propagation. The process thus can afford the substitution of a poor electron-donor nucleophile through an entrainment reaction, which is also a support for the chain nature of the reaction.

Because the $S_{RN}1$ is a chain mechanism, the overall reactivity depends on the efficiency of the initiation, propagation, and termination steps. The initiation step may be slow; nevertheless, for the process to work efficiently, the chain propagation must be fast and feasible to allow for long chains to build up.

The magnitude of the chain length of any $S_{RN}1$ reaction can easily be derived from the overall quantum yield by determining the initiation quantum yield. The latter could be obtained when the propagation cycle is eliminated or reduced significantly in comparison with the initiation step. For instance, a quantum yield of 0.127 was determined for substitution of neophyl iodide by the enolate anion of acetophenone.[4] The quantum yield of initiation, evaluated by the suppression of the propagation steps with the presence of the radical trap di-*tert*-butylnitroxide (DTBN), has a value of 10^{-3}. On this basis, the chain length or $\Phi_{propagation}$ obtained for the reaction is ca. 127. This is the first report of $\Phi_{propagation}$ for an $S_{RN}1$ process, demonstrating that overall quantum yields below 1 cannot be taken as a criterion against a chain.

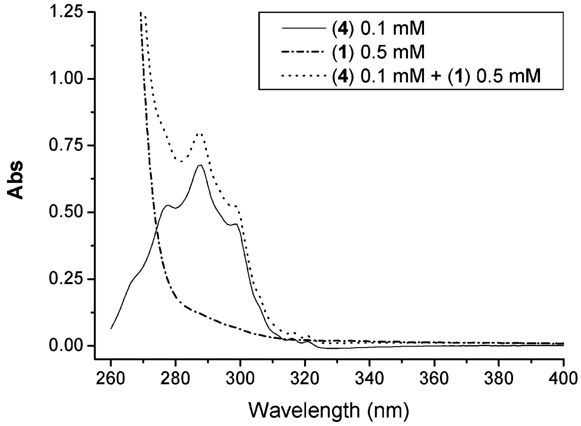


FIGURE 1. UV−vis spectra of **4** and anion **1** in DMSO.

We have described for the first time the reactivity of sulfur-centered nucleophiles such as thiourea anion[11] and thioacetate anion[12] in photoinduced aromatic $S_{RN}1$ as a "one-pot" method for the synthesis of several sulfur aromatic compounds from moderate to good yields. The use of commercially available, easily handled thiourea, potassium *tert*-butoxide, and thioacetate salts, and the mild conditions (room temperature under nitrogen atmosphere in DMSO), make this process a very convenient methodology for obtaining aryl thiols, alkyl aryl sulfides, symmetrical or unsymmetrical diaryl sulfides, and diaryl disulfides (Scheme 2).

Moreover, with hydrogen abstraction from DMSO as a clock reaction, the absolute rate constants for the addition of S^{2-}, thiourea, and benzene thiolate anions to 1-naphthyl radicals have been measured. The values obtained are 0.5×10^9, 1.0×10^9, and 5.1×10^9 M^{-1} s^{-1}, respectively.[13]

Even though the reactivity of thiourea and thioacetate anions in the reactions with aryl halides is quite similar, these nucleophiles show a very different behavior at the initiation step.[11,12] The advantage of these reactions for the synthesis of sulfur compounds together with the scarce information available on the photoinduced initiation and the propagation steps have prompted us to study the mechanism of these photostimulated reactions. Therefore, we report herein the reactivity of thiourea (**1**), thioacetate (**2**), and thiobenzoate (**3**) anions versus 1-naphthyl radicals and a comparative and detailed study of the photoinduced electron-transfer pathway at the initiation level and their reactivity in the propagation steps. We have also measured the quantum yields and the chain length for the propagation cycle of these $S_{RN}1$ reactions and provided evidence for the identity of the chain carriers.

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[13] Argüello, J. E.; Schmidt, L. C.; Peñéñory, A. B. *Arkivoc* **2003**, Part (x), 411−419.

TABLE 1. Reactions of Sulfur-Centered Nucleophiles with 1-Bromonaphthalene (4) in DMSO[a]

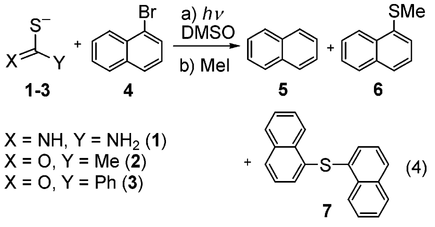
				product yield (%)[c]			
entry	"S"$^-$	conditions time (min)	comp. added[b]	convn	**5**	**6**	**7**
1[d,e]	**1**	180, dark					
2[d,e]		15, $h\nu$		91	9	48	19
3[d,e]		15, $h\nu$	DTBN	25	2	9	8
4	**2**	180, $h\nu$					
5[f]		15, $h\nu$		92	3	48	34
6[f]		15, $h\nu$	*p*-DNB				
7[f]		15, $h\nu$	DTBN	22	<2	8.5	5
8[f]		15, $h\nu$	TEMPO	39	12	11	39
9	**3**	90, $h\nu$					
10[f]		90, $h\nu$		72	3	39	34
11[f]		180, $h\nu$		100	4	43	31

[a] ArX = **4**, 0.05 M; "S"$^-$ sulfur-centered nucleophiles, 0.25 M. After irradiation under nitrogen atmosphere, the reaction was quenched by MeI. [b] Compounds added 0.01 M. [c] Determined by GC using the internal standard method, error 5%. The conversion (convn) was determined by quantification of the recovered substrate. [d] Nucleophile/**4** ratio of 10:1. [e] From ref 11. [f] Together with 0.1 M *t*-BuOK.

Results

Reactions of the Sulfur-Centered Nucleophiles 1, 2, and 3 with 1-Bromonaphthalene (4). Table 1 summarizes the results obtained for anions **1**, **2**, and **3** in their photoinduced reactions with bromide **4**.

The photostimulated reaction of anion **1** with **4** after quenching with MeI renders naphthalene (**5**, 9%), 1-(methylthio)-naphthalene (**6**, 48%), and bis(1-naphthyl) sulfide (**7**, 19%) (eq 4). This reaction does not occur in the dark and is inhibited in the presence of a very efficient radical trap like DTBN (Table 1, entries 1, 2, and 3).



(4)

The thioacetate anion (**2**) was unreactive toward **4** as electron-donor under photostimulation, but in the presence of potassium *tert*-butoxide (*t*-BuOK) and under irradiation (entrainment conditions), they gave **5** (3%), and sulfides **6** (48%) and **7** (34%) after quenching with MeI (Table 1, entries 4 and 5).

This photoinduced reaction is completely suppressed by the addition of a good electron-acceptor such as *p*-dinitrobenzene (*p*-DNB) (Table 1, entry 6) and is significantly inhibited by the presence of radical scavengers like DTBN and TEMPO (Table 1, entries 7 and 8).

Nucleophile **3** fails to react with **4** even after 1.5 h of irradiation (Table 1, entry 9). Although the expected products **5**, **6**, and **7** are obtained under entrainment conditions, the global reactivity of anion **3** is lower as compared to those of anions **1** and **2** (Table 1, entries 10 and 11).

Photoinduced Initiation Step and Laser Flash Photolysis Measurements. To gain a better understanding of the photoinduced initiation step, the photophysical properties of **4** are studied in the presence and absence of anion **1**. Nucleophiles **2** and **3** were not considered because they are not able to initiate the reaction. By contrast, the base used for the formation of the nucleophiles, *t*-BuOK, also the entrainment reactant in the reactions of anions **2** and **3**, is taken into consideration in this photophysical study.

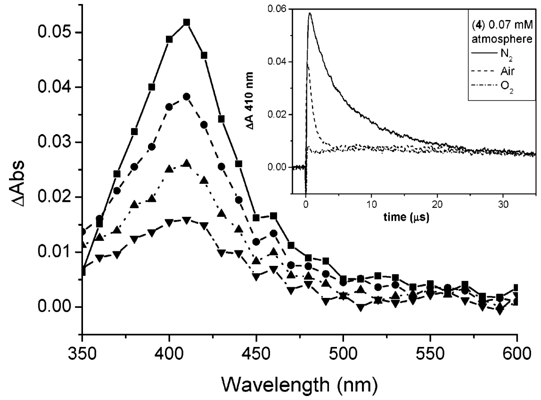


FIGURE 2. Transient absorption spectrum of **4** 0.07 mM in DMSO: (■) 1 μs, (●) 3 μs, (▲) 7.5 μs, and (▼) 15 μs after the laser pulse. Inset: Quenching effect of oxygen measured at 410 nm.

Bromide **4** absorbs maximally at 290 nm, whereas nucleophile **1** shows absorption below 280 nm (Figure 1). No charge complex interaction could be detected by the UV−vis absorption spectrum, **4** being mainly responsible for the photon absorption in the preparative experiments.[14] As a result, we have focused on the photophysical properties of **4** to understand the nature of the photoinduced initiation step of the reaction mechanism. The photophysics of naphthalene derivatives is well-known, and in the case of bromonaphthalenes they are not significantly dependent on the solvent employed.[15] As it is expected, 1-bromonaphthalene shows very weak fluorescence with a quantum yield value of 0.002 in DMSO. A strong absorption band with a maximum at 410 nm and a lifetime (τ) of 8 μs is observed by laser flash photolysis (LFP) using Nd:YAG laser operating at 266 nm (Figure 2). The reported value for the triplet−triplet (T−T) absorption of **4** in acetonitrile is 420 nm.[15] This would indicate that the transient observed can be assigned as a T−T band for the triplet excited state of **4** in DMSO; the latter is confirmed by the strong quenching effect showed by the presence of molecular oxygen (inset in Figure 2). A value close to unity is estimated for the triplet quantum yield of **4** in DMSO as compared to naphthalene, considering the reported extinction coefficient value.[16]

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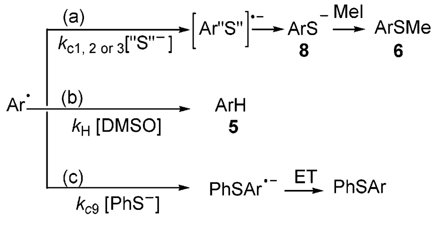
SCHEME 3



Ar = 1-naphthyl; "S"$^-$ = **1**, **2** or **3**

It was not possible to detect any transient absorption when the nucleophiles studied were added to a solution of **4**. On the other hand, a dynamic quenching of the triplet state of **4** is achieved by addition of *t*-BuOK in concentration over 0.10 mM. The quenching constant rate value was (4.6 ± 0.5) × 10^8 M^{-1} s^{-1} from the slope in a plot of τ^{-1} against *t*-BuOK concentration. Neutral thiourea has no effect on the triplet lifetime of **4**, and the reactivity of the anion **1** was difficult to measure because of the interference of *t*-BuOK used as a base for the anion formation. Contrary to our expectation, the addition of thiourea to a solution of **4** with an excess of *t*-BuOK results in an increase in the lifetime of the triplet state of **4**. This unusual observation is ascribed to the diminution of the concentration of *t*-BuOK concomitant with the addition of thiourea, as *t*-BuOK is more reactive than anion **1** toward the triplet state of **4**. The value of the slope from a plot of τ^{-1} versus the concentration of anion **1** is the same, but negative, as that determined for *t*-BuOK, confirming the reactivity observed. A rough value of (8 ± 7) × 10^7 M^{-1} s^{-1} for the triplet state quenching by anion **1** could be estimated using NaOMe as a base.

Determination of the Rate Constant for Nucleophilic Addition. From the reaction in Table 1, it is clear that anions **1** and **2** have similar reactivity toward 1-naphthyl radicals. Even though the whole reaction for anion **3** is slower, the product distributions are similar to those observed for anions **1** and **2**. Considering that the $S_{RN}1$ process comprises initiation, propagation, and termination steps, it was interesting to evaluate the relative reactivity of anions **1**, **2**, and **3** toward 1-naphthyl radicals in competitive experiments. Because the three nucleophiles render the same product, 1-naphthalene thiolate ion (**8**), we choose benzene thiolate anion (**9**) as a partner to carry out separated competitive reactions, and to avoid the further competition for 1-naphthyl radicals by anion **8**, which would finally give product **7**.

In addition, the absolute rate constants for the coupling (k_c) of 1-naphthyl radicals with anions **1**, **2**, **3**, and **9** can be determined in DMSO using hydrogen abstraction from the solvent as competitive reaction, whose rate constant k_H has a value of 7.1 × 10^6 M^{-1} s^{-1} at 25 °C.[17] Three competitive reaction pathways can take place for the intermediate aryl radicals as outlined in Scheme 3: pathway (a), coupling with anions **1**, **2**, or **3** to yield the substitution product 1-naphthalene thiolate anion (**8**) after electron-transfer or fragmentation; pathway (b), hydrogen abstraction from the solvent DMSO to render the reduction product naphthalene; and pathway (c), coupling with the benzene thiolate anion (**9**) to afford the substitution product (1-naphthyl) phenyl sulfide after electron-transfer.

TABLE 2. Rate Constant (k_c) for the Reaction of 1-Naphthyl Radical with Sulfur-Centered Nucleophiles in DMSO at 25 °C[a]

entry	"S"$^-$ (M)	$k_{c\mathbf{9}}/k_{c\text{“S”}}$	k_c[b] 10^9 (M^{-1} s^{-1})
1	**1**, 0.50	5	1.0
2	**2**, 0.25	4.56	1.42
3[c]	**2**, 0.25	5.19	0.98
4	**3**, 0.25	2.40	
5[c]	**3**, 0.25	2.51	3.5

[a] Photostimulation at 300 nm in 10 mL of DMSO, irradiation time 60 min. Anion benzene thiolate (**9**), 0.125 M; **4**, 0.05 M. Product yield determined by GC using the internal standard method. [b] From duplicated experiments: average error ≤10%. [c] Together with 0.1 M *t*-BuOK. [d] Not quantified.

TABLE 3. Quantum Yields and Chain Lengths of the PET Reactions of 4 with Sulfur-Centered Nucleophiles[a]

		ϕ_{products}[b]				
entry	"S"$^-$	**5**	**6**	**7**	ϕ_{global}[b]	chain length
1	**1**	0.22	1.68	0.37	2.27	7.7 ± 1.4[e]
2[c]	**1**	0.25	2.01	0.39	2.65	
3[d]	**1**	0.44	0.91		1.35	
4[c]	**2**	0.19	1.02	0.12	1.33	4.9 ± 0.5[f]
5[c]	**3**	0.10	0.07		0.17	no chain
6[c]		0.27			0.27	

[a] Performed under nitrogen atmosphere, using 0.05 M solutions of substrate and 0.50 M solutions of the nucleophiles. [b] Determined at $\lambda_{\max}$ 300 nm, from duplicated experiments: average error ≤10%. [c] In the presence of *t*-BuOK 0.1 M. [d] In the presence of 0.25 M of 1,4-cyclohexadiene. [e] Calculated from the intercept of Figure 3 (using equation chain length = $k_{Nu}[Nu^-]/(k_H[DMSO] + k_{H'}[C_6H_8])$). [f] Calculated by eq 7 from the Discussion.

Once the yields from the substitution (**6** and PhSAr) and reduction (**5**) products were determined in the photoinduced reactions of 1-bromonaphthalene with anions **1**, **2**, **3**, and **9** in excess, it was possible to calculate the k_c using eq 5 and the relative reactivities using eq 6 (Table 2).[18] For ion **9**, we obtained from the competitive experiments with **1**, **2**, or **3** similar values for $k_{c\mathbf{9}}$, with an average value of (6 ± 2) × 10^9 M^{-1} s^{-1}.

$$\frac{k_c}{k_H} = \frac{[\mathrm{ArNu}]_t[\mathrm{DMSO}]}{[\mathrm{ArH}]_t[\mathrm{Nu}^-]_o} \tag{5}$$

$$\frac{k_{c\mathbf{9}}}{k_{c\mathbf{1,2}\mathrm{or}\mathbf{3}}} = \frac{[\mathrm{ArSPh}]_t[\text{“S”}^-]_o}{[\mathrm{ArSMe}]_t[\mathbf{9}]_o} \tag{6}$$

Quantum Yield Measurements. The quantum yields (λ = 300 nm) for the reactions between **4** and anions **1**, **2**, and **3** were determined between 0.17 and 2.65. A total quantum yield of 2.27 was obtained in the reaction with **1**, which can be improved to 2.65 with the addition of *t*-BuOK as initiator. Using 1,4-cyclohexadiene (C_6H_8) as a radical scavenger, the product **7** is not observed, and the quantum yield drops to 1.35 (Table 3). With increasing amounts of 1,4-cyclohexadiene from 0.1 to 0.4 M, the ratio $\Phi\mathbf{5}/\Phi\mathbf{6}$ increases linearly with the concentration of the radical scavenger with a slope = (1.85 ± 0.09) and the intercept = (0.13 ± 0.02) (Figure 3). The slope of this plot represents the ratio between the hydrogen abstraction rate

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(18) $[Nu^-]_o$ is the initial concentration of the nucleophile; ArH and ArNu are the concentrations of the reduction and substitution products at time *t*. These equations are based on the assumption that the reactions of the aryl radicals with the nucleophiles and the solvent are first order in the latter species, and their concentrations are constant during the experiments.

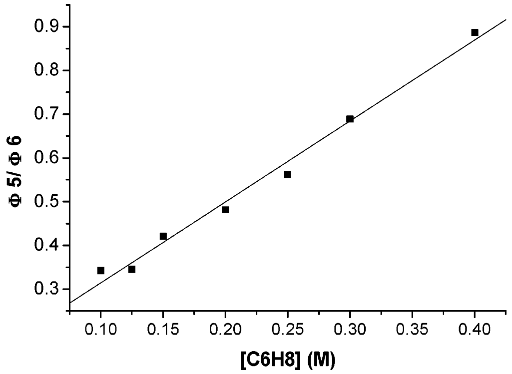


FIGURE 3. Quantum yield ratio determined at λ_{max} 300 nm for the reaction of **1** (0.5 M) and **4** (0.05 M) under nitrogen atmosphere with variable concentrations of 1,4-cyclohexadiene (C_6H_8).

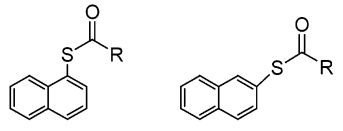
constant of 1-naphthyl radical from 1,4-cyclohexadiene and the addition rate constant to **1** (see discussion below, Figure 3).[19]

For anions **2** and **3**, the global quantum yields were 1.33 and 0.17, respectively, both in the presence of *t*-BuOK as electron-transfer donor (Table 3). The PET reaction between *t*-BuOK and bromide **4** only yields naphthalene as product with a quantum yield of 0.27 (Table 3).

Electrochemical Reduction of 1- and 2-Naphthalenethiol Acetate and Benzoate. Electrochemical investigations have been carried out in DMSO at room temperature; for preparative purposes, 2-naphthalenethiol, acetate (**10b**), and 2-naphthalenethiol, benzoate (**11b**), were used instead of 1-substituted derivatives. In the electrochemical reduction of 1- and 2-substituted naphthalene derivatives, it has been reported that neither the reduction potential nor the fragmentation rate constant is significantly dependent on the substituted position.[20] For this reason, results from compounds **10b** and **11b** are considered equivalent to **10a** and **11a** (Chart 1).

In cyclic voltammetry, the two naphthalenethioesters show one reduction peak. In the case of **11b**, the peak measured at a sweep rate faster than 5 V/s can be assigned to a one-electron diffusion-controlled reversible process, with a standard reduction potential value of −1.64 V.

CHART 1



R = Me (**10a**) R = Me (**10b**)
R = Ph (**11a**) R = Ph (**11b**)

A different behavior was observed for compound **10b**, whose cyclic voltammetry shows a single one-electron irreversible reduction peak in the available potential window, with a peak potential $E_p = -2.08$ V vs SCE at 0.2 V/s. The irreversibility remained the same up to the maximum sweep rate accessible (100 V/s).[21] The E_p for **10b**, even after 21 mV correction, does not represent the E^0 value because of the irreversibility of the peak. However, because the cyclic voltammetric data are consistent with an electrochemical reductive cleavage involving the intermediacy of the anion radical, it can be inferred that the standard potential of the **10b**/**10b**$^{\bullet-}$ couple must be more negative than the effective reduction potential. Accordingly, the E_p value represents an upper limit for E^0.

Discussion

A detailed mechanistic study of the photochemical substitution reaction between thiourea (**1**), thioacetate (**2**), and thiobenzoate anions (**3**) with **4** was performed in DMSO. We evaluated the PET initiation, the addition rate constants of the nucleophiles to the 1-naphthyl radical, the efficiency of the initiation and propagation steps (the chain length), as well as the nature of the chain carrier in the propagation steps.

Nucleophilic Substitution Reactions of 1-Bromonaphthalene with Anions 1, 2, and 3. Mechanism for the PET Reductions of 4 and Rate Constant for Nucleophilic Addition. Nucleophiles **1**, **2**, and **3** react under photostimulation with **4** to afford products **5**, **6**, and **7** after addition of MeI. Anion **1** is able to initiate the reaction and add to the 1-naphthyl radical, while anions **2** and **3** are not reactive at the PET initiation step toward **4** and *t*-BuOK was necessary as entrainment reactant. The presence of naphthalene as a side product and its enhancement by the addition of a well-known hydrogen donor such as 1,4-cyclohexadiene are evidence for 1-naphthyl radicals as reactive intermediates in these reactions.

All of these results together with the inhibition experiments suggest that the reactions studied proceed by a radical chain $S_{RN}1$ mechanism (Scheme 1). This process comprises a photoinduced initiation step, a radical addition of the 1-naphthyl radical to the nucleophiles **1**, **2**, or **3**, propagation, and termination steps.[1]

The three sulfur nucleophiles studied showed different reactivity in the initiation and propagation steps of the $S_{RN}1$ process. The PET from the anion to **4** depends mainly on the oxidation potential of the anion, which is its ability as electron-donor.

Bordwell et al. have developed linear correlations of rates of ET reactions with pK_{HA} values. For example, linear plots of E_{ox} (A^-) versus pK_{HA} with slopes near unity establish the presence of an intrinsic relationship between oxidation potentials of carbanions and their equilibrium acidities in DMSO. They showed that an increase in the ion basicity there is an E_{ox} (A^-) shift to a more negative potential. In general, it has been observed that the higher is the pK_{HA}, the higher is the electron-donor capability of its conjugated base and so the higher is the probability of a spontaneous ET reaction.[22]

Our experimental data clearly show that the weaker bases thioacetate and thiobenzoate anions are not able to transfer one-electron to the acceptor 1-bromonaphthalene even under pho-

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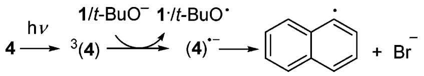
(19) Because product **7** is not observed in these reactions and assuming steady state for the intermediates in the $S_{RN}1$ mechanism, $(\Phi ArH)/(\Phi ArSMe) = (k_H[DMSO])/(k_c[\text{“S”}]) + (k_{H'}[C_6H_8])/(k_c[\text{“S”}])$.

(20) Costentin, C.; Robert, M.; Savèant, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 16051−16057.

(21) At a low and moderate sweep rate (0.05−1 V/s), E_p varied linearly with the logarithm of the sweep rate by 45 mV per unit on average with a peak width $E_{p/2} - E_p = 65$ mV on average. These values are typical of an "EC" mechanism with a mixed kinetic control by E (electron-transfer processes with the formation of the anion radical) and C (first-order cleavage of the anion radical) steps. From these electrochemical experiments, the reductive cleavage of **10b** would follow a stepwise mechanism involving the intermediacy of the anion radical. For references, see: Andrieux, C. P.; Le Gorande, A.; Savèant, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 6892−6904 and references cited therein.

(22) (a) Bordwell, F. G.; Zhang, X. *Acc. Chem. Res.* **1993**, *26*, 510−517. (b) Bordwell, F. G.; Zhang, X.; Filler, R. *J. Org. Chem.* **1993**, *58*, 6067−6071. (c) Bordwell, F. G.; Clemens, A. H.; Smith, D. E.; Begemann, J. *J. Org. Chem.* **1985**, *50*, 1151−1156.

SCHEME 4



toestimulation and need an additional source of electrons to initiate the reaction, while thiourea anion behaves as a good electron-donor under the same experimental conditions. (The pK_a values in DMSO are PhCOSH, 5.2;[23] MeCOSH, undetermined;[24] and thiourea, 21.1.[23b]) Furthermore, other thiolate anions such as alkanethiolate anions (pK_a from 17.9 to 10.3 for t-BuSH to PhCH$_2$SH, respectively),[23c] sulfide anion (pK_a HS$^-$: 13), and benzene thiolate anion (pK_a PhSH: 10.3) are able to transfer one-electron to aryl halides and react by the $S_{RN}1$ mechanism.[1a,b] On the other hand, thiocyanate anion (pK_a NCSH: 4) is not reactive both at initiation and at propagation steps.[13] Thus, the behavior observed for sulfur-centered nucleophiles resembles the reactivity of ketone enolate carbanions in comparison with nitronate anions in $S_{RN}1$ reactions. While ketone enolates anions are able to transfer one-electron to ArX to initiate an $S_{RN}1$ mechanism, nitromethane anions require entrainment conditions to react under irradiation.[25] (The pK_a values in DMSO are acetone, 26.5; acetophenone, 24.7; and nitromethane, 17.2.[23b])

Finally, both thioacetate and thiobenzoate anions are reactive by thermal ET when a better electron-acceptor such as the diazonium tetrafluoroborates derivative is used.[26]

The nature of the PET (initiation step) was studied by means of UV spectroscopy and LFP. There is no evidence of the formation of a CTC between the nucleophile **1** and the bromide **4**, which allows us to disregard this possibility as a mechanism for the ET reaction. Furthermore, quenching studies by LFP clearly indicate that the triplet state of **4** is responsible for the ET reaction with **1** and t-BuOK, giving **4**$^{\bullet -}$ as a reactive intermediate.[27] Fragmentation[28] of the latter renders the 1-naphthyl radical and bromide ion (Scheme 4).

The quenching rate constant values determined for anion **1** and t-BuOK (0.8×10^8 and 4.6×10^8 M^{-1} s^{-1}, respectively) are evidence for a quite efficient process with a quantum yield of approximately 0.3. The photoinduced reaction between t-BuOK and **4** only affords the reduction product naphthalene. For this anion, which is only reactive at the initiation step, the quantum yield for the formation of naphthalene can be taken as an approximate value for the efficiency of the initiation step.[4]

The preparative photolysis experiments show a similar overall reactivity for anions **1** and **2**. Anion **3** also gives a product ratio comparable to that of anions **1** and **2**, although the reaction is slower, requiring much longer irradiation time for a quantitative conversion of **4**. This distinct behavior indicates differences between the nature of the chain propagation steps. For nonactivated aromatic halides, the coupling reaction between the nucleophile and the radical is the most important step in determining whether an $S_{RN}1$ process takes place. If this reaction cannot compete efficiently with the termination steps, the chain will be short, or even nonexistent.

The rate constants for the addition of the nucleophiles studied to the 1-naphthyl radical were determined by means of the hydrogen atom abstraction from DMSO as competitive reaction. Hence, the rate constant measured for thiourea anion (1.0×10^9 M^{-1} s^{-1}) is comparable to the value obtained in liquid ammonia toward 4-cyanophenyl radical (4.2×10^9 M^{-1} s^{-1}).[29] Taking anion **1** as a reference, the following reactivity order is obtained: $^-$SC(NH)NH$_2$ (**1**) 1.00, MeCOS$^-$ (**2**) 1.2, PhCOS$^-$ (**3**) 3.5, and PhS$^-$ (**9**) 5. This order is in agreement with the expected one from the stability of the radical anion formed in the addition step. The reversible reduction of **11b** by cyclic voltammetry indicates that the electrochemical radical anion formed (**11b**$^{\bullet -}$) is stable at the time scale of the voltammetric experiments. On the other hand, an irreversible process is observed for the reduction of **10b** at the maximum sweep rate accessible (100 V/s). Extra delocalization of the unpaired electron over the phenyl ring leads to stabilization of the corresponding radical anion for **11b**.

With a similar strategy, Galli and co-workers have measured the rate constant for the addition of the pinacolone enolate anion to 9-anthracenyl and 1-naphthyl radicals (4.4×10^8 and 2.9×10^9 M^{-1} s^{-1}, respectively),[30a] and, more recently, the coupling of various nucleophiles to vinyl radicals has been investigated.[30b] In general, the addition of nucleophiles to aryl radicals, other than the simplest phenyl radicals, is a very fast reaction ranging from 10^8 to 10^{10} M^{-1} s^{-1}.[1]

The differences in the global reactivity found for anions **1**, **2**, and **3** cannot be explained in terms of the coupling between 1-naphthyl radical and the corresponding anion given that these anions show similar addition rate constants (between 1 and 3.5 $\times 10^9$ M^{-1} s^{-1}). Moreover, anion **3**, which shows the minor overall reactivity, adds faster to the naphthyl radicals. Therefore, the differences in reactivity are given by their ability of building up a chain, which is strongly dependent on the anion employed.

Chain Propagation Steps: Efficiency and Chain Carrier. The quantum yield measured for substitution (Φ_{global}) depends both on the efficiency of initiation and on the turnover in the propagation steps. A nucleophile may be reactive both at the initiation step and in the coupling reaction with the radical (anion **1**), only as initiator (t-BuOK), at the propagation cycle (anion **2**), or at the addition step (anion **3**). A good approximation for calculating the magnitude of the chain length ($\Phi_{\text{propagation}}$) of

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[23] (a) Courtot-Coupez, J.; Le Demezet, M. *Bull. Soc. Chim. Fr.* **1969**, 1033−1039. (b) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463. (c) Bordwell pK_a table: www.chem.wisc.edu/areas/reich/pkatable/.

[24] The pK_a of MeCOSH should be 1 or 2 pK units higher than the value of PhCOSH.

[25] Borosky, G. L.; Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1992**, *57*, 247−252.

[26] (a) Petrillo, G.; Novi, M.; Garbarino, G.; Filiberti, M. *Tetrahedron* **1989**, *45*, 7411−7420. (b) Petrillo, G.; Novi, M.; Garbarino, G.; Filiberti, M. *Tetrahedron Lett.* **1988**, *29*, 4185−4188.

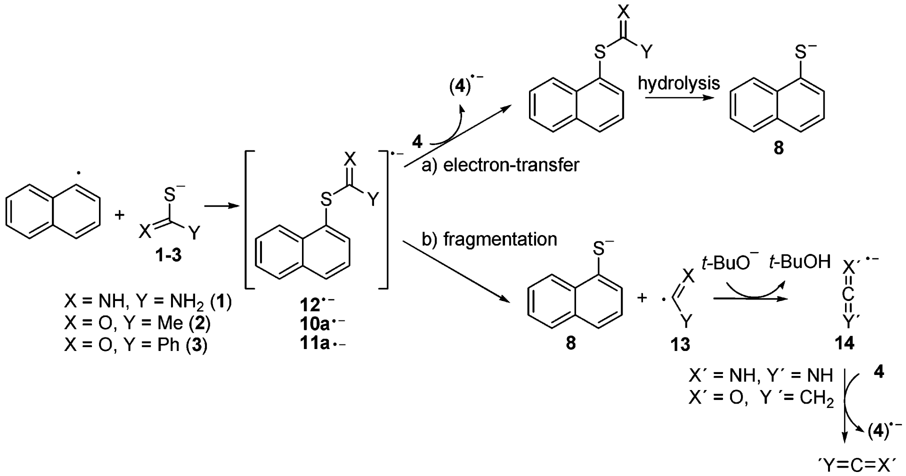
[27] In general, a stepwise process with consecutive ET and fragmentation of the C−X bond is proposed for aromatic halides in which the radical anion is an intermediate. By quenching studies of the fluorescent excited state of 2-naphthoxide ion by aromatic halides, we have proposed a concerted ET mechanism (C−X, BDE control) for bromo- and iodobenzene, whereas 1-bromonaphthalene exhibits a stepwise process (π LUMO control).[7] Whereas a change from concerted to stepwise was observed by changing the scan rate for PhI, PhBr and 1-iodonaphthalene follow a stepwise mechanism over the whole range of scan rate under electrochemical initiation. (a) Pause, L.; Robert, M.; Saveant, J.-M. *J. Am. Chem. Soc.* **1999**, *121*, 7158−7159. On the other hand, despite the lower driving force exerted under homogeneous relative to that under electrochemical reduction, a stepwise mechanism has been proposed for the reduction of PhI by different radical anions. (b) Enemaerke, R. J.; Christensen, T. B.; Jensen, H.; Daasbjerg, K. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 1620−1630.

[28] The cleavage rate constants for ArX have been determined in DMSO, and for 1-bromonaphthalene it is around 2×10^8 s^{-1}. M'Halla, F.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1980**, *102*, 4120−4127.

[29] Combellas, C.; Dellerue, S.; Mathey, G.; Thiébault, A. *Tetrahedron Lett.* **1997**, *38*, 539−42.

[30] (a) Annunziata, A.; Galli, C.; Marinelli, M.; Pau, T. *Eur. J. Org. Chem.* **2001**, 1323−1329. (b) Branchi, B.; Galli, C.; Gentili, P. *Eur. J. Org. Chem.* **2002**, 2844−2854.

SCHEME 5



any $S_{RN}1$ reaction is by the ratio of the overall quantum yield and the quantum yield of the initiation step (eq 7).[4] The latter could be obtained provided that the propagation cycle is eliminated or reduced significantly in comparison with the initiation step.

$$\text{chain length} = \Phi_{\text{propagation}} = \Phi_{\text{global}}/\Phi_{\text{initiation}} \qquad (7)$$

Table 2 shows quantum yields higher than the unity for the reactions of anions **1** and **2**. These results indicate that the substitution reactions occur by a radical chain reaction and for anion **1** the addition of 1,4-cyclohexadiene quenches the formation of product **7** but **6** remains present, although in lower yield. The chain lengths for the reaction of bromide **4** with theses anions can be estimated using different approaches. In the case of anion **1**, because suppression of the substitution product **6** cannot be achieved even at concentration of the radical scavenger up to 0.4 M, the chain length for the reaction with this anion can be estimated from the intercept in Figure 3. The reciprocal of the intercept would represent the ratio $k_{Nu}[Nu^-]/(k_H[DMSO] + k_{H'}[C_6H_8])$ that accounts for the ratio between the propagation and the termination steps in the $S_{RN}1$ mechanism. Considering this approximation, an estimated value around 8 can be calculated for the chain length of the reaction between **4** and anion **1**. The case of anion **2** is simpler. Because this anion is not able to initiate the reaction, eq 7 can be used to calculate the chain length. In consequence, with the overall quantum yield of 1.33 and assuming the value of 0.27 as the initiation quantum yield (*t*-BuOK alone), a chain length value around 5 can be estimated for the reaction with anion **2**.

The low quantum yield determined for the reaction between anion **3** and **4** may suggest that the process is not a chain reaction or that the addition step with 1-naphthyl radical is very slow or that the initiation is not efficient. These last two assumptions can be easily ruled out. First, good conversion is achieved at longer irradiation time and the reduction product naphthalene is formed in very low yields (Table 1), which is stated by the measurements of the addition rate constants of 1-naphthyl radical toward anions **1**, **2**, and **3** in competitive experiments (Table 2). Second, the use of an entrainment reagent such as *t*-BuOK provides a quite efficient initiation step.

On this basis, the chain length or rather the existence of a chain for these reactions depends on the efficiency of the propagation steps in relation to the possible termination pathways. To account for the results obtained herein, the mechanism outlined in Scheme 5 is proposed. Addition of 1-naphthyl radical to anions **1**, **2**, or **3** yields the corresponding radical anion $(\mathbf{10-12})^{\bullet-}$. Two competitive reactions are possible for the latter: in pathway (a), $(\mathbf{10-12})^{\bullet-}$ transfer their odd electron to bromide **4**, which is the common step to continue the propagation cycle of an $S_{RN}1$ mechanism; in pathway (b), fragmentation of $(\mathbf{10-12})^{\bullet-}$ gives the 1-naphthalenethiolate anion (**8**) and the radical **13** (i.e., formamidinyl, acetyl, or benzoyl depending on the nucleophile). For the first two radicals, deprotonation mainly by the *t*-BuOK or anion **1** can afford the radical anion **14**. This radical anion is able to transfer the odd electron to **4** to allow for a chain to build up.[31] In the case of anion **3**, the fragmentation pathway (b) leads to the benzoyl radical (**13**, Y = Ph, X = O), which has no acidic hydrogen. As a consequence, this fragmentation affords a further unreactive benzoyl radical and becomes a termination step.

Pathway (a) has been suggested for the reactions of anions **2** and **3** with the arenediazonium tetrafluoroborates in aprotic solvent, leading to the corresponding aryl thioesters as final product in moderate to high yields.[26] Therefore, by treatment of the potassium thioacetate or sodium thiobenzoate salts with 1-naphthyl-N_2^+, the corresponding thioesters could be isolated in up to 60% and 70% yield, respectively. In these reactions, once the naphthalene thioester radical anion $(\mathbf{10-11})^{\bullet-}$ is formed, ET to the arenediazonium salts is considerably fast (pathway a) so that the fragmentation is not a competitive reaction. This mechanism is consistent with the electrochemical properties of the arenediazonium salts, which are powerful electron-acceptors.[32] For example, most of them have positive reduction potential and are employed for electrode surface modifications.[33]

For the bromide derivative, the reaction follows pathway (b) of the mechanism in Scheme 5.[34] The detection of the fragmentation product rather than the thioester derivatives and the reaction quantum yield over the unity strongly support the occurrence of pathway (b). This step involves fragmentation of the radical anions $(\mathbf{10-12})^{\bullet-}$ and the possibility of building up

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(31) Another possibility would be the formation of new radical anions by coupling of anions **1**, **2**, or **3** with radical **13**, which are able to continue with the propagation cycle. The absence of chain propagation and the fact that not even traces of PhCOSCOPh were observed for anion **3** allow us to disregard this possibility.

(32) Allongue, P.; Delamar, M.; Desbat, B.; Fagebaumme, O.; Hitmi, R.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1997**, *119*, 201−207.

(33) Pinson, J.; Podvorica, F. *Chem. Soc. Rev.* **2005**, *34*, 429−439.

TABLE 4. Calculated $\Delta G_{ET}{}^0$ (kcal mol^{-1}) for the ET Reaction between 4, 1-Naphtahlene Diazonium Salt (1-NaphN$_2{}^+$), and Radical Anions 10b and 11b

thioester	**4**	1-naphN$_2{}^+$
10b$^{\bullet-}$	6.2	−41.3
11b$^{\bullet-}$	11.5	−36.0

a chain when deprotonation of the radical **13** is likely. However, the feasibility of process (b) is worth verifying on thermodynamic grounds by evaluating the relative driving force of the ET reaction between the donor radical anions (**10a**$^{\bullet-}$ and **11a**$^{\bullet-}$) and the acceptor 1-bromonaphthalene. The free energy change $\Delta G_{ET}{}^0$ for the ET from an electron-donor D to an electron-acceptor A is given by eq 8 when E^0 (D$^{\bullet+}$/D) and E^0 (A/A$^{\bullet-}$) are the standard potentials of the appropriate redox couples, respectively, and ΔE_{coul} is the Coulombic interaction energy for the two singly charged radical ions formed in the SET process.

$$\Delta G_{ET}{}^0\ (\text{kcal mol}^{-1}) = 23.06\ [E^0\,(\text{D}^{\bullet+}/\text{D}) - E^0\,(\text{A}/\text{A}^{\bullet-})] - \Delta E_{coul} \quad (8)$$

Because reaction would occur between a radical anion donor (**10a** or **11a**) and a neutral molecule (**4**) giving the corresponding neutral naphthalene thioester and 1-bromonaphthalene radical anion, the Coulombic interaction (ΔE_{coul}) that is necessary to separate opposite charged fragments is not considered.

The $\Delta G_{ET}{}^0$ value for the SET reaction can thus be calculated using the redox potential of compounds **10b** and **11b** (used as a model for compounds **10a** and **11a**, see the above results) and the 1-bromonaphthalene available in the literature.[20] Although the E^0 value for **10b** is approximated, qualitative information on the driving force of the reaction can be achieved. The $\Delta G_{ET}{}^0$ values calculated on this basis are reported in Table 4.[35] From the $\Delta G_{ET}{}^0$ values collected in Table 4, it results that the reaction involving the more stable **11b**$^{\bullet-}$ is highly endergonic, while for **10b**$^{\bullet-}$ its fragmentation is faster (see the electrochemical results) and the reaction with 1-bromonaphthalene is also endergonic. These results are also in agreement with a fragmentation process followed by proton-transfer and electron-transfer as outlined in pathway (b), which is the more plausible step to account for a chain reaction, while a direct ET process (pathway a) is highly unlikely for bromide **4** (Scheme 5).

Conclusion

1-Bromonaphthalene (**4**) reacts with thiourea (**1**), thioacetate (**2**), and thiobenzoate (**3**) anions by a photoinduced radical substitution reaction to afford 1-(methylthio)naphthalene (**6**) as a main product together with bis(1-naphthyl) sulfide (**7**) and naphthalene (**5**) after quenching with MeI. The aryl thioesters are not intermediate products in these reactions because the radical anion fragments into two reactive species: 1-naphthalene thiolate anion and a new radical. In the case of anions **1** and **2**, the latter radical is able to continue with the propagation accounting for a chain length; see below.

Quenching of the triplet state of **4** was assigned as the photoinduced initiation step, where the triplet excited state of **4** acts as a better electron-acceptor toward anion **1** and the entrainment reactant *t*-BuOK. Anions **2** and **3** need an entrainment reagent in agreement with the expected reducing power and the pK_a values of the conjugated acids. For their corresponding bases, the lower is the pK_a, the more positive is the oxidation potential.

The absolute rate constants determined for the addition of anions **1**, **2**, and **3** to 1-naphthyl radicals are 1.0×10^9, 1.2×10^9, and 3.5×10^9 M^{-1} s^{-1}, respectively, and the reactivity order, $k_{Nu\mathbf{3}} > k_{Nu\mathbf{2}} \cong k_{Nu\mathbf{1}}$, is in agreement with the stability of the resulting radical anions (ArNu)$^{\bullet-}$.

Even anion **3** is the most reactive in the addition step; the global reaction is the least efficient as compared to anions **1** or **2**. This can be explained taking into account the nature of the chain propagation of the reaction.

The inhibition experiments of the photoinduced substitution reaction in the presence of radical scavengers and the global quantum yield higher than the unity are evidence of a radical chain mechanism for the substitution reactions by anions **1** and **2**. Anion **3** adds to 1-naphthyl radical, but it is neither able to initiate the reaction nor to keep the propagation cycle. Positive values of the ET driving forces for the reaction between (ArNu)$^{\bullet-}$ and **4** together with the absence of a chain reaction for the anion **3** indicate that the propagation step is given by an acid−base reaction between the radical $^{\cdot}$C(O)Me or $^{\cdot}$C(NH)-NH$_2$ and a base to afford (O═C═CH$_2$)$^{\bullet-}$ or (HN═C═NH)$^{\bullet-}$ that transfer their odd electron to **4**, continuing the chain.

Experimental Section

Chemicals. *t*-BuOK, SC(NH$_2$)$_2$, MeCOSK and PhCOSH, 1-bromonaphthalene, naphthalene, thiophenol, *p*-dinitrobenzene, TEMPO, and DTBN were all high-purity commercial samples, which were used without further purification. DMSO was distilled under vacuum and stored over molecular sieves (4 Å). Anions **1**, **3**, and PhS$^-$ were generated in situ by acid−base deprotonation using *t*-BuOK. 2- Naphthalenethiol, acetate (**10b**), and 2-naphthalenethiol, benzoate (**11b**), were synthesized by reaction between 2-naphthalenetiol and acetyl or benzoyl chloride.[36]

All products are known and exhibited physical properties identical to those reported in the literature. Also, they were isolated by radial chromatography from the reaction mixture and characterized by ^{1}H and ^{13}C NMR and mass spectrometry.

Registry no.: 1-(methylthio)naphthalene,[37] [10075-72-6]; bis(1-naphthyl) sulfide,[38] [607-53-4]; 1-naphthyl phenyl sulfide,[39] [7570-98-1]; 2-naphthalenethiol, acetate,[36] [831-23-2]; 2-naphthalenethiol, benzoate,[40] [10154-60-6].

Instrumentation. Time-Resolved Absorption Spectroscopy. The laser flash photolysis system was based on a pulsed Nd:YAG

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(34) When the reaction is performed with an excess of 1-bromonaphthalene, it was possible to observe 1-naphthalenethiol, acetate (**10a**) (see ref 12). This clearly supports the competition between ET and fragmentation steps as shown in Scheme 5. Furthermore, if ArSCOMe was an intermediate in these reactions, we would be able to trap it by an intramolecular reaction with an amino or hydroxy group ortho to the leaving group. In the photoinduced reaction of *o*-amino-iodobenzene with thioacetate anion, followed by addition of MeI, the only products observed were ArSMe with the amino group mono- and di-methylated without any traces of the benzenethiazole derivative.

(35) It should be emphasized that the relative value to **10b** must be considered a lower limit in view of the preceding considerations. Therefore, the actual $DG_{ET}{}^0$ value for the ET reaction with 1-bromonaphthalene should be larger than that reported in Table 4.

(36) Penn, J. H.; Liu, F. *J. Org. Chem.* **1994**, *59*, 2608−2612.

(37) Gilman, H.; Webb, F. J. *J. Am. Chem. Soc.* **1949**, *71*, 4062−4066.

(38) Hauptmann, H.; Wladislaw, B. *J. Am. Chem. Soc.* **1950**, *72*, 710−712.

(39) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173−3174.

(40) Chen, C.-T.; Kuo, J.-H.; Pawar, V. D.; Munot, Y. S.; Weng, S.-S.; Ku, C.-H.; Liu, C.-Y. *J. Org. Chem.* **2005**, *70*, 1188−1197.

laser, using 266 nm radiation as the excitation wavelength. The single pulses were of ca. 10 ns duration, and the energy was ca. 20 mJ/pulse. A Xe lamp was employed as the detecting light source. The laser flash photolysis apparatus consisted of the pulsed laser, the Xe lamp, a monochromator, a photomultiplier (PMT) system, and oscilloscope. The output signal of the oscilloscope was transferred to a personal computer for study.

Electrochemistry. The working electrode was a 3 mm-diameter glassy carbon electrode disk that was carefully polished and ultrasonically rinsed in absolute ethanol before use. The counter electrode was a platinum wire, and the reference electrode was an aqueous SCE electrode. All experiments have been done at 20 °C. Cyclic voltammetric data were recorded using a commercial computer-controlled potentiostat.

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Supporting Information Available: General methods, completed Table 2, quenching of the triplet of **4** by *t*-BuOK, and cyclic voltammograms of **10b** and **11b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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