DOI: 10.1002/ejoc.200500955

Photoinduced Nucleophilic Substitution of Aryl Halides with Potassium Thioacetate – A One-Pot Approach to Aryl Methyl and Diaryl Sulfides

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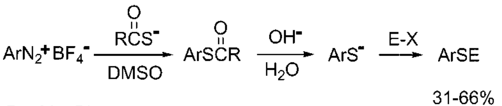
Keywords: Electron transfer / Nucleophilic substitution / Sulfides / Radical anions / Radicals

Aryl methyl sulfides and diaryl sulfides were prepared by photoinduced reactions of potassium thioacetate with aryl halides under entrainment conditions. Without isolation, the arene thiolates obtained by the aromatic substitution were quenched with methyl iodide to afford the aryl methyl sulfides in 26–59 % yields in a "one-pot" procedure together with the diaryl sulfides in variable yields (3–31 %). By optimization of the reaction conditions it was possible to improve the formation of the Ar_2S, going from moderate to good yields (64–83 %).

Introduction

Aryl sulfides are widely used as intermediates in organic synthesis,[1] and numerous synthetic methods for their preparation have been developed. Polar aromatic nucleophilic substitutions by HS^- or RS^- anions required strong ring activation by electron-withdrawing groups (EWGs).[2] For non-activated aryl halides the use of transition metal catalysis, high temperatures, and long reaction times are necessary.[3,4] Sulfides have also been synthesized by cross-coupling reactions of aryl boronic acid or aryl triflates with thiols.[5] Alternatively, the synthesis of aryl sulfides is possible by reduction of sulfoxides and sulfones,[6] or by treatment of organolithium or Grignard compounds with elemental sulfur,[7] while a one-pot synthesis of alkyl aryl sulfides through reactions between alkyl halides and lithium arene thiolates prepared in situ has also been recently reported.[8]

Sulfur-centered nucleophiles such as thiolate anions have been shown to react with non-activated aryl halides under photostimulation conditions to yield new C–S bonds by radical nucleophilic substitution ($S_{RN}1$ mechanism) involving electron transfer pathways.[9] While arene thiolate anions (ArS^-) afford good yields of substitution products, alkane thiolate anions (RS^-) yield mixtures of products arising from fragmentation of the radical anion intermediates and straightforward substitution (scrambling products), making these reactions disadvantageous for synthetic purpose.[10] However, the expected straightforward substitution is mainly achieved with compounds bearing EWGs or with polycyclic or heterocyclic halides.[11] Thioacetate and thiobenzoate anions react with arenediazonium tetrafluoroborates to provide the corresponding aryl thio esters in moderate yields, and hydrolysis to the arene thiolates and further treatment with electrophiles provides access to other aromatic sulfur derivatives [Equation (1)].[12] The reactions with thioacetate and thiobenzoate anions were attributed to a radical nucleophilic substitution mechanism, which implies the handling of the usually unstable diazonium salts, and the yields of the sulfur compounds were modest.



$$\mathrm{ArN_2^+BF_4^-} \xrightarrow[\text{DMSO}]{\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{S^-}} \mathrm{ArS}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R} \xrightarrow[\mathrm{H_2O}]{\mathrm{OH^-}} \mathrm{ArS^-} \xrightarrow{\text{E-X}} \underset{31\text{-}66\%}{\mathrm{ArSE}} \qquad (1)$$

R = Me, Ph

Ar = Ph, 3-MeC_6H_4, 4-$MeOC_6H_4$, 1-naphthyl

E-X = HX, MeI, BzCl, 2,4-$(NO_2)_2C_6H_3Cl$, ICN

We have recently reported on the reactivity of the thiourea anion in photoinduced aromatic radical nucleophilic substitution as a "one-pot" method for the synthesis of aryl thiols, alkyl aryl sulfides, symmetrical or unsymmetrical diaryl sulfides, and diaryl disulfides in moderate to good yields.[13] Furthermore, through the use of hydrogen abstraction from DMSO as competitive reaction, the absolute rate constants for the addition of S^{2-}, $^{-}SCNH(NH_2)$, and benzenethiolate anions to 1-naphthyl radicals were determined to be $0.5{\cdot}10^9\ \mathrm{M^{-1}\,s^{-1}}$, $1.0{\cdot}10^9\ \mathrm{M^{-1}\,s^{-1}}$, and $5.1{\cdot}10^9\ \mathrm{M^{-1}\,s^{-1}}$ respectively.[14] These results encouraged us to explore further the reactivity and the potential of related sulfur anions for the synthesis of aromatic sulfur compounds. Here we report the "one-pot" synthesis of aryl methyl and symmetrical diaryl sulfides by photoinduced reactions between thioacetate anion (**1**) and haloarenes in the presence of appropriate initiators in DMSO.

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Results and Discussion

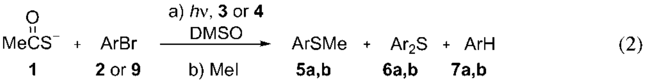
Table 1 summarizes the results obtained in the photoinduced reactions between anion **1** and 1-bromonaphthalene (**2**) in the presence of *tert*-butoxide anion (**3**) or the enolate anion of cyclohexenone (**4**) as entrainment reagents[9] and after quenching with methyl iodide.

Table 1. Photoinduced reactions between anion **1** with 1-bromonaphthalene (**2**) and 4-bromobiphenyl (**9**).[a]

Entry	ArX	Ratio ArX/**1**	Products yield [%][b] Convn.	MB	ArH	ArSMe	Ar_2S
1[c]	**2**	1:10	–	–	–	–	–
2		1:10	85	71	6	40	14
3[d]		1:10	91	59	5	35	14
4		1:5	85	68	6	40	12
5[e][f]		2:1	53	93	8	–	32[g]
6[f]	**9**	1:5	100	90	21	38	31
7[f][h]		1:5	44	52	12	11	–
8[f][i]		1:5	36	64	10	6	7
9[j]		1:5	100	91	41	27	23

[a] ArX: 0.05 M, *t*BuO⁻ (**3**) equimolar with the anion **1**, after 3 h of irradiation under nitrogen atmosphere; the reaction was quenched with MeI. [b] Determined by GC by the internal standard method, error <5%. Conversion (convn.) was determined by quantification of the unreacted substrate. Mass balance (MB). [c] In the absence of the entrainment reagents **3** or **4**. [d] In the presence of **4**. [e] ArX: 0.25 M. [f] Irradiation time1 h. [g] Together with 9% of 1-naphthyl thioacetate (**8a**). [h] In the presence of 0.01 M of *p*-dinitrobenzene. [i] In the presence of 0.01 M DTBN. [j] Reaction performed in liquid ammonia, with ArX: 0.02 M.

There is no reaction between anion **1** and **2** alone (**2**/**1** ratio of 1:10) under irradiation. When the photoinduced reaction (λ_{max} = 365 nm) was performed in the presence of the anions **3** or **4** (good electron donors),[15] it gave 1-(methylthio)naphthalene (**5a**) (40%), di(1-naphthyl) sulfide (**6a**) (14%), and naphthalene (**7a**) (6%) [Equation (2)]. Similar results were obtained when the reaction was performed with only a fivefold excess of anion **1** relative to **2** (Table 1, Entries 1–4). Because of the low recovery of naphthalene after three hours of irradiation, the mass balances in these reactions were around 70%.

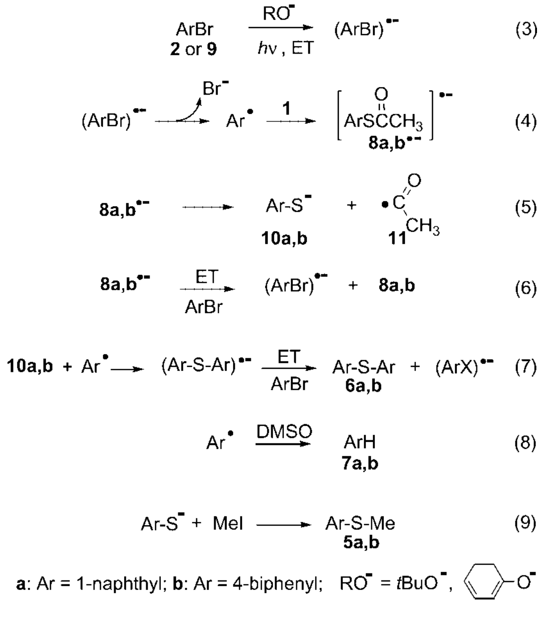


$$\underset{\mathbf{1}}{\mathrm{Me\overset{O}{\overset{\|}{C}}S^-}} + \underset{\mathbf{2}\text{ or }\mathbf{9}}{\mathrm{ArBr}} \xrightarrow[\text{b) MeI}]{\text{a) }h\nu,\ \mathbf{3}\text{ or }\mathbf{4}\text{, DMSO}} \underset{\mathbf{5a,b}}{\mathrm{ArSMe}} + \underset{\mathbf{6a,b}}{\mathrm{Ar_2S}} + \underset{\mathbf{7a,b}}{\mathrm{ArH}} \qquad (2)$$

a: Ar = 1-naphthyl; **b**: Ar = 4-biphenyl

Finally, with a **2**/**1** ratio of 2:1 and an increased concentration of **2** (0.25 M), it was possible to obtain 1-naphthyl thioacetate (**8a**) as intermediate product together with sulfide **6a** (Table 1, Entry 5). To study the reaction mechanism further, we explored the reactivity of 4-bromobiphenyl (**9**) with anion **1** in the presence of anion **3** under irradiation conditions. After 1 h conversion was complete, the reaction afforded a 38% yield of the 4-MeS-substituted product **5b**, a 31% yield of the diaryl sulfide **6b**, and a 21% yield of biphenyl (**7b**) [Equation (2)] This photoinduced reaction was strongly inhibited by the addition of a very efficient radical trap such as di-*tert*-butylnitroxide (DTBN) or a good electron acceptor such as *p*-dinitrobenzene (*p*-DNB) (Table 1, Entries 6–8). The reaction between anion **1** and **2** under entrainment conditions did not occur in the dark. The yield of biphenyl was considerably increased when the photochemical reaction of 4-bromobiphenyl was conducted in liquid ammonia as solvent (Table 1, Entry 9).

The lack of reaction between anion **1** and **2** alone under irradiation conditions, the entrainment reaction in the presence of anions **3** or **4** under light catalysis conditions for both aryl halides **2** and **9**, the strong inhibition of the latter reaction between anion **1** and bromide **9** by DTBN or *p*-DNB, and the formation of **8a** and naphthalene or biphenyl as reduction products are all evidence of a radical chain mechanism for these substitution reactions, and can be interpreted as follows (Scheme 1). Thioacetate anions are poor electron donors[16] and they are unable to transfer one electron to the aryl halide to initiate the reaction under irradiation conditions. On the other hand, photoinduced electron transfer (PET) from anions **3** or **4** to the aryl halide affords the corresponding radical anion [see Equation (3) in Scheme 1]. Fragmentation of this radical anion yields the aryl radical, which is not reactive towards anions **3** or **4**, and can only couple with anion **1** to generate the radical anion $\mathbf{8}^{\bullet-}$ [Equation (4) in Scheme 1]. Two competitive reactions are possible for the latter: fragmentation of $\mathbf{8}^{\bullet-}$ to afford the thiolate anion **10** and the radical **11** [Equation (5) in Scheme 1], or ET to the aryl halide to afford product **8** and the radical anion of the aryl halide [Equation (6) in Scheme 1]. The formation of **8a** when the reaction is performed with **2** in excess confirmed this step and the participation of anion **1** as the nucleophilic species responsible for the introduction of the sulfur atom.



Scheme 1.

This competition is not observed when the aryl diazonium salts are used instead of ArX, because they are easily reduced. In these reactions, ET from $\mathbf{8}^{\bullet-}$ to the aryl diazonium salts provides the aryl thioacetate as final product. Our results therefore clearly reveal different behavior for thioacetate anion with aryl halides in photoinduced reactions under entrainment conditions, compared to thermal reactions with the diazonium salts.[12]

The arene thiolate anion **10**, formed in the reaction media, is able to add to the aryl radical to yield the disubstitution product **6** after ET to the substrate, following a new cycle of the $S_{RN}1$ reaction [Equation (7) in Scheme 1]. Finally, by hydrogen atom abstraction from the solvent, the aryl radical gives the corresponding aromatic hydrocarbon (**7**) as reduction product [Equation (8) in Scheme 1]. After irradiation, the reaction mixture was quenched with methyl iodide to afford the 1-(methylthio) aryl derivatives **5** [Equation (9) in Scheme 1]. As has been previously proposed for the PET reactions with thiourea anion,[13] two different pathways to account for the chain reaction are possible. Coupling of radical **11** with anion **1** present in excess would form a new radical anion capable of continuing with the chain propagation. Another possibility is deprotonation of **11** to afford the radical anion $[H_2C{=}C{=}O]^{-\cdot}$, which could continue the $S_{RN}1$ cycle by ET to the aryl halide. In any case, the products after ET would probably be water-soluble and hydrolyze during workup.

Anion **1** thus clearly shows a different reactivity from thiourea anion. While the anion **1** is not reactive as electron donor under photostimulation conditions[16] and needs an additional source of electrons to initiate the reaction, but is reactive in coupling with the aryl radicals, the thiourea anion is reactive in both pathways.[13] This is consistent with the pK_a value of thiourea in DMSO (21.1).[17]

Finally, the possibility of a coupling reaction between $^{\cdot}SCOMe$ and $Ar^{\cdot}$ to afford Ar–SCOMe,[12] can be disregarded because of the followings factors: a) there is no source of $^{\cdot}SCOMe$ radical under the reaction conditions, as thioacetate anion is not able to transfer one electron to the substrate to produce the aryl halide radical anion and the $^{\cdot}SCOMe$ radical, b) the fact that 1-naphthyl thioacetate (**8a**) is only observed when the reaction is performed with an excess of 1-bromonaphthalene clearly supports competition between ET and fragmentation steps as stated in Equation (5) and (6) (Scheme 1), and c) we were unable to trap the Ar–SCOMe through intramolecular reaction with amino or hydroxy groups *ortho* to the leaving group, the only products observed in the photoinduced reaction between 2-iodoaniline and anion **1**, followed by addition of MeI, being ArSMe with the amino group mono- and dimethylated without any traces of the benzenethiazole derivative.

We further explored the reactivity of anion **1** with a variety of aryl halides in photoinduced reactions, and Table 2 condenses the results obtained. In general, the thioacetate anions are less reactive than the arene thiolate anions generated in the reaction media, and these reactions yield a mixture of both the mono- and disubstitution products (ArSMe and Ar_2S respectively) after quenching with MeI. From Table 2 it is possible to conclude that this methodology is appropriate for non-activated aryl bromides or iodides (chlorides are not reactive) and substrates bearing both electron-donating and electron-withdrawing groups. In these cases, the arene thiolate anions obtained by the $S_{RN}1$ reaction were quenched with MeI to afford the ArSMe derivatives in moderate to good yields (26–59%) together with the Ar_2S in variable yields (3–31%).

Table 2. Photoinduced reactions between anion **1** and aryl halides.[a]

Entry	ArX		Product yields [%][b]		
		Convn.	ArH	ArSMe	Ar_2S
1	1-Br-naphthalene	85	6	40	12
2[c]	2-Br-naphthalene	100	5	43	27
3	PhI	100	[d]	56	3
4	4-IC_6H_4Me	100	[d]	46	16
5	2-IC_6H_4Me	100	[d]	59	–
6	4-IC_6H_4OMe	100	28	41	6
7	2-IC_6H_4OMe	100	17	50	–
8	4-BrC_6H_4SMe	100	6	37	29
9 [c]	4-BrC_6H_4CN	100	–	41	12
10	4-$IC_6H_4NO_2$	100	–	51 (49)[f]	–
11	4-$PhCOC_6H_4Br$	100	–	42 (41)[f]	[d]
12[c]	2-$MeCOC_6H_4Br$	100	–	26	17
13[e]	4-Br-C_6H_4-C_6H_5	100	21 (20)[f]	38 (38)[f]	31
14	9-Br-anthracene	98	12	50	[d]
15	9-Br-phenanthrene	93	8	46	[d]

[a] ArX: 0.05 M, **1**: 0.25 M, *t*BuO⁻ (**3**) equimolar to the anion **1**; the reaction was quenched with MeI after irradiation for 3 h under nitrogen in DMSO. [b] Determined by GC by the internal standard method, error <5%. The conversion (convn.) was determined by quantification of the unreacted substrate. [c] In the presence of enolate anion **4** as entrainment reagent. [d] Not quantified. [e] Irradiation time 1 h. [f] Isolated yield.

In variations of the reaction conditions, ArX/nucleophile ratio and concentration were adjusted in order to improve the yields of either ArSMe or Ar_2S (Table 3). Because of the higher reactivity of the arene thiolate anions formed in these reactions in comparison with the thioacetate anion, the yields of the ArSMe increased moderately with changes in the reaction conditions. Thus, with a **2/1** ratio of 1:10 and a 0.025 M concentration of **2**, the yield of 1-(methylthio) naphthalene (**5a**) increased up to 55% after 3 h, and the mass balance improved. (Table 3, Entry 1). Good yields of the ArSMe were obtained when the intermediate thiolate anions were sterically hindered (Table 3, Entries 2 and 3).

Conversely, it was also possible to improve the yields of Ar_2S preferentially by optimization of the reaction conditions. With a **2/1** ratio of 1:1, the photoinduced reaction between **2** (0.125 M) and anion **1** gave a 42% yield of bis (1-naphthyl) sulfide (**6a**) as the major product after 3 h. This yield could be improved to 83% by increasing the concentration to 0.25 M with a **2/1** ratio of 1:0.6 (Table 3, Entries 4 and 5). Thus, by use of appropriate reaction conditions it was possible to obtain the symmetrical diaryl sulfides in yields of up to 83% in a one-pot procedure. Under conditions optimized to afford the symmetrical diaryl sulfide preferentially, the photoinduced reaction between **2** and thiourea anion afforded only a 38% yield of the bis (1-naphthyl) sulfide.[13] This is valuable for the use of thioacetate anion instead of thiourea anion in the synthesis of sym-

Table 3. One-pot syntheses of aryl methyl sulfides or diaryl sulfides.[a]

Entry	ArX	Ratio ArX/**1**	Product yields [%][b] ArH	ArSMe	Ar_2S
1[c]	1-Br-naphthalene	1:10	9	55	22
2	2-IC_6H_4OMe	1:10	7	70	9
3	2-IC_6H_4Me	1:10	[d]	79	9
4[e]	1-Br-naphthalene	1:1	10	10	42
5	1-Br-naphthalene	1:0.6	8	3	83
6	PhI	1:0.6	[d]	5	64
7	4-BrC_6H_4CN	1:0.6	6	12	33
8	4-Br-C_6H_4-C_6H_5	1:0.6	17	5	46

[a] ArX: 0.25 M, *t*BuO$^-$ (**3**) equimolar to the anion **1**, the reaction was quenched with MeI after irradiation for 3 h under nitrogen in DMSO. The conversion was complete in all cases. [b] Determined by GC by the internal standard method, error <5%. [c] ArX: 0.025 M. [d] Not quantified. [e] ArX: 0.125 M.

metrical diaryl sulfides. Table 3 condenses the results obtained.

This methodology has some advantages over the previously reported reactions between thioacetate anions and aryl diazonium salts: a) hydrolysis of the aryl thioacetate to yield the arenethiolates, desirable for further reactions, is not necessary, b) aryl halides are commercially available and easier to handle than the usually unstable diazonium salts, and c) the production of arene thiolate anions in the reaction media, which can further react with the aryl radicals, allows the symmetrical diaryl sulfides to be obtained in high yields in one-pot procedures. With aryl halides containing EWGs, the arene thiolate anions obtained are less reactive that the thioacetate anion in the coupling reactions with the radical, and as a result of such competition the diaryl sulfide is obtained in low yield. In spite of this limitation, the possibility to synthesize, for example, bis[4-(cyano) phenyl] sulfide in a one-pot procedure starting with commercially available reagents in 3 h is very convenient. Alternative synthesis of these compounds required the use of arylmagnesium halides or aryllithium at very low temperatures, or metal catalysis reactions. These procedures imply a more tedious workup or require the use of expensive catalysts, and are sensitive to the presence of EWGs such as –CN, –NO_2 or –COR.

Conclusion

We describe for the first time the reactivity of thioacetate anions as nucleophiles in photoinduced reactions with aryl halides under entrainment conditions, for the synthesis of aryl methyl and especially for symmetrical diaryl sulfides.

This novel reaction is a very simple and convenient methodology for a one-pot synthesis of sulfides in moderate to good yields, involving the use of commercially available potassium *tert*-butoxide and thioacetate salts under very mild conditions.

Experimental Section

General Methods: Irradiation was conducted with a 125-W medium-pressure Hg lamp with its emission maximum at 365 nm (Applied Photophysics Limited). ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Bruker AC 200 spectrometer, and all spectra are reported in δ (ppm) relative to Me_4Si, with $CDCl_3$ as solvent. Gas chromatographic analyses were performed on a Hewlett–Packard 6890 A instrument with a flame-ionization detector, either on a HP-5 30 m capillary column of 0.32 mm × 0.25 µm film thickness or on a HP1 5 m × 0.53 × 2.65 µm film thickness column. GC/MS analyses were carried out on a Shimadzu GC-MS QP 5050 spectrometer, with a 25 m × 0.2 mm × 0.33 µm HP-5 column.

Materials: *t*BuOK, potassium thioacetate, cyclohexenone, the aryl halides, naphthalene, DTBN, thioanisole, diphenyl sulfide, 1-methoxy-4-(methylthio)benzene, 4-(methylthio)nitrobenzene, and 4-(methylthio)benzonitrile were all high purity commercial samples, used without further purification. DMSO was purified by standard procedures and stored over molecular sieves (4 Å). The cyclohexenone enolate anion (**4**) was generated in situ by acid-base deprotonation with *t*BuOK. All the reaction products were isolated from the reaction mixture by radial chromatography and characterized by ^1H and ^{13}C NMR and mass spectrometry. These sulfides are known and had physical properties identical to those reported in the literature.

Representative Experimental Procedure: The reactions were carried out in a 10 mL three-necked Schlenk tube, fitted with nitrogen gas inlet and magnetic stirrer. The tube was dried under vacuum, filled with nitrogen, and then loaded with dried DMSO (10 mL). *t*BuOK (280.5 mg, 2.5 mmol), potassium thioacetate (285.5 mg, 2.5 mmol), and the aryl halide (0.5 mmol), were added to the degassed solvent under nitrogen. After 3 h of irradiation with a medium-pressure Hg lamp with maximum emission at 365 nm, the reaction was quenched by addition of methyl iodide (342 µL, 5.5 mmol) and water (30 mL), and the mixture was then extracted with dichloromethane (3 × 20 mL). The organic extract was washed twice with water and dried with anhydrous $MgSO_4$, and the products were quantified by GC by the internal standard method or were isolated from the crude product reaction mixture by radial chromatography.

1-(Methylthio)naphthalene:[18] Liquid. ^1H NMR (200 MHz, $CDCl_3$, 30 °C): δ = 2.60 (s, 3 H, SMe), 7.40–7.75 (m, 5 H, Ar–H), 7.84–7.89 (m, 1 H, Ar–H), 8.31–8.36 (ddd, *J* = 5.9, 2.2, 0.7 Hz, Ar–H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 30 °C): δ = 16.2, 123.7, 124.3, 125.6, 125.8, 126.1, 126.2, 128.5, 131.7, 133.6, 135.8 ppm.

Di(1-naphthyl) Sulfide:[19] Liquid. ^1H NMR (200 MHz, $CDCl_3$, 30 °C): δ = 7.32–7.96 (m, 14 H, Ar–H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 30 °C): δ = 126.2, 126.7, 127.4, 127.7, 128.6, 128.9, 129.8, 132.3, 133.1, 133.8 ppm.

1,4-Bis(methylthio)benzene:[20] Solid, m.p. 78–79 °C (ref.[20] 78–79 °C). ^1H NMR (200 MHz, $CDCl_3$, 30 °C): δ = 2.45 (s, 6 H, 2 × SMe), 7.19 (s, 4 H, Ar–H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 30 °C): δ = 16.4, 127.6, 135.2 ppm.

2-(Methylthio)acetophenone:[21] Solid, m.p. 44–45 °C (ref.[21] 45–47 °C). ^1H NMR (200 MHz, $CDCl_3$, 30 °C): δ = 2.43 (s, 3 H, SMe), 2.61 (s, 3 H, CH_3) 7.15–7.34 (m, 2 H, Ar–H), 7.43–7.51 (ddd, *J* = 7.7, 7.5, 1.1 Hz, 1 H, Ar–H), 7.81–7.86 (dd, *J* = 7.7, 1.1 Hz, 1 H, Ar–H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 30 °C): δ = 15.8, 28.1, 123.3, 124.9, 131.0, 132.2, 134.3, 142.5, 198.9 ppm.

4-(Methylthio)benzophenone:[22] Solid, m.p. 75–76 °C. ^1H NMR (200 MHz, $CDCl_3$, 30 °C): δ = 2.52 (s, 3 H), 7.26–7.31 (m, 2 H), 7.42–7.57 (m, 3 H), 7.71–7.79 (m, 4 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$, 30 °C): δ = 14.8, 124.8, 128.2, 129.7, 130.6, 132.1, 133.6, 137.8, 145.2, 195.7 ppm.

Chem. Abstr. Registry Numbers: 1-(Methylthio)naphthalene[18] [10075-72-6], 2-(methylthio)naphthalene[23] [7433-79-6], di(1-naphthyl) sulfide[19] [607-53-4], di(2-naphthyl) sulfide[24] [613-81-0], 2-(methylthio)acetophenone[21] [1441-97-0], 4-(methylthio)benzophenone[22] [23405-48-3], 1,4-bis(methylthio)benzene[20] [699-20-7], bis[4-(methylthio)phenyl] sulfide[20] [125877-23-8], 4-(methylthio)toluene[25] [623-13-2], di(4-tolyl) sulfide[12b] [620-94-0], 2-(methylthio)toluene[26] [14092-00-3], bis[4-(methoxy)phenyl] sulfide[13] [3393-77-9], 1-methoxy-2-(methylthio)benzene[11] [2388-73-0], bis[4-(cyano)phenyl] sulfide[13], 4-(methylthio)biphenyl[27], di(biphenyl) sulfide [6554-57-0], 9-(methylthio)anthracene[28], 9-(methylthio)phenanthrene[29] [120972-30-7].

Acknowledgments

This work was supported partly by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and FONCYT, Argentina. L. C. S. and V. R. gratefully acknowledge receipt of a fellowship from CONICET.

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[1] a) R. J. Cremlyn, *An Introduction to Organosulfur Chemistry*; John Wiley & Sons, Chichester, **1996**; b) D. N. Jones, *Comprehensive Organic Chemistry* (Eds.: D. H. Barton, D. W. Ollis); Pergamon, New York, **1979**; vol. 3.

[2] M. B. Smith and J. March, *March's Advanced Organic Chemistry*, 5th ed., John Wiley & Sons, New York, **2001**, p. 863.

[3] Pd catalysis: a) T. Migita, T. Shimizu, Y. Asami, J.-I. Shiobara, Y. Kato, M. Kosugi, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1385–1389; b) G. Y. Li, G. Zheng, A. F. Noonan, *J. Org. Chem.* **2001**, *66*, 8677–8681.

[4] Cu catalysis: a) J. Lindley, *Tetrahedron* **1984**, *40*, 1433–1456; b) W. Deng, Y. Zou, Y.-F. Wang, L. Liu, Q.-X. Guo, *Synlett* **2004**, 1254–1258; c) Y.-J. Wu, H. He, *Synlett* **2003**, 1789–1790; d) F. Y. Kwong, S. L. Buchwald, *Org. Lett.* **2002**, *4*, 3517–3520; e) C. G. Bates, R. K. Gujadhur, D. Venkataraman, *Org. Lett.* **2002**, *4*, 2803–2806.

[5] a) C. Savarin, J. Srogl, L. S. Liebeskind, *Org. Lett.* **2002**, *4*, 4309–4312; b) P. S. Herradura, K. A. Pendola, R. K. Guy, *Org. Lett.* **2000**, *2*, 2019–2022; c) N. Zheng, J. C. McWilliams, F. J. Fleitz, J. D. Armstrong III, R. P. Volante, *J. Org. Chem.* **1998**, *63*, 9606–9607.

[6] a) ref.[2] p. 1557; b) M. Madesclaire, *Tetrahedron* **1988**, *44*, 6537–6580.

[7] J. L. Wardell, in: *The Chemistry of the Thiol Group* (Ed.: S. Patai), part 1, Wiley, New York, **1974**, p. 211.

[8] J. Ham, I. Yang, H. Kang, *J. Org. Chem.* **2004**, *69*, 3236–3239.

[9] a) R. A. Rossi, A. B. Pierini, A. B. Peñéñory, *Chem. Rev.* **2003**, *103*, 71–167; b) R. A. Rossi, A. B. Pierini, A. N. Santiago, in: *Organic Reactions* (Eds.: L. A. Paquette, R. Bittman); John Wiley & Sons, Inc. **1999**, pp. 1–271.

[10] R. A. Rossi, S. M. Palacios, *J. Org. Chem.* **1981**, *46*, 5300–5304.

[11] R. Beugelmans, M. Bois-Choussy, B. Boudet, *Tetrahedron* **1983**, *39*, 4153–4161.

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

[13] J. E. Argüello, L. C. Schmidt, A. B. Peñéñory, *Org. Lett.* **2003**, *5*, 4133–4136.

[14] J. E. Argüello, L. C. Schmidt, A. B. Peñéñory, *Arkivoc* **2003**, 411–419.

[15] *tert*-Butoxide anion and the enolate anion of cyclohexenone are able to transfer one electron to aryl halides to initiate an $S_{RN}1$ reaction, but they are not reactive in propagation (addition to aryl radicals). This feature makes these anions suitable entrainment anions for $S_{RN}1$ reactions. J. E. Argüello, A. B. Peñéñory, R. A. Rossi, *J. Org. Chem.* **2000**, *65*, 7175–7182.

[16] The pK_a of MeCOSH should be one or two pK units higher than the value for PhCOSH (pK_a = 5.2 in DMSO). J. Courtot-Coupez, M. Le Demezet, *Bull. Soc. Chim. Fr.* **1969**, 1033–1039.

[17] F. G. Bordwell, *Acc. Chem. Res.* **1988**, *21*, 456–463.

[18] H. Gilman, F. J. Webb, *J. Am. Chem. Soc.* **1949**, *71*, 4062–4066.

[19] H. Hauptmann, B. Wladislaw, *J. Am. Chem. Soc.* **1950**, *72*, 710–712.

[20] K. Kobayashi, E. Koyama, K. Namatame, T. Kitaura, C. Kono, M. Goto, T. Obinata, N. Furukawa, *J. Org. Chem.* **1999**, *64*, 3190–3195.

[21] R. J. Crawford, C. Woo, *J. Org. Chem.* **1966**, *31*, 1655–1656.

[22] A. Mustafá, *J. Chem. Soc.* **1949**, 352–355.

[23] a) Ng. Ph. Buu-Hoi, Ng. Hoán, D. Lavit, *J. Chem. Soc.* **1953**, 485–489; b) J. Jacques, *Bull. Soc. Chim. Fr.* **1955**, 231–236.

[24] H. Hauptmann, B. Wladislaw, *J. Am. Chem. Soc.* **1950**, *72*, 707–709.

[25] A. Mc Curdy, L. Jimenez, D. A. Stauffer, D. A. Dougherty, *J. Am. Chem. Soc.* **1992**, *114*, 10314–10321.

[26] K. Smith, C. M. Lindsay, G. J. Pritchard, *J. Am. Chem. Soc.* **1989**, *111*, 665–669.

[27] G. Y. Li, *J. Org. Chem.* **2002**, *67*, 3643–3650.

[28] F. D. Saeva, D. T. Breslin, *J. Org. Chem.* **1989**, *54*, 712–714.

[29] H. Sakuraba, K. Natori, Y. Tanaka, *J. Org. Chem.* **1991**, *56*, 4124–4129.

Received: December 6, 2005