96. Reactions of Haloarenes with Thiolate Anions in Tetraglyme: Competition between Electron Transfer and S_NAr Mechanisms

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The reaction of the bromo-substituted naphthalene **1** with the alkanethiolate anions **2a–b** and arenethiolate **2c** in tetraglyme gave the corresponding 1-naphthyl thio-ethers **3a–c**. Thio-ethers **3a–c** were oxidized to the corresponding sulfones **4a–c** with *m*-chloroperoxybenzoic acid. The reaction of the dichloro-substituted anthracene **5a** with **2b** gave the disubstitution product **6a**. The reaction of 9-bromoanthracene **5c** with the alkanethiolate **2b** gave **6b**, whereas the reaction of **5c** with the arenethiolate **2c** gave a mixture of substitution product **6c** and anthracene **7**. The observation of the formation of both **6c** and **7** is explained by the competition between substitution (S_NAr) and electron-transfer (ET) mechanisms. Consistent with this interpretation, the reaction of the monochloro-substituted **5b**, which has a higher-energy σ^* orbital, with **2c** gave **6c** without the formation of **7**. Zn/KOH in tetraglyme was shown to reduce the aryl halides **5b–c** and thio-ether **6c** to **7**.

Introduction. – Considerable research effort continues towards the development of methodologies for the substitution of aryl halides by thiolate anions because the substitution products are currently of considerable theoretical interest. Alkyl- and arylthiobenzenes, for example, have been used in the design of inclusion compounds [1]. Recent advances in the technology of organic metal conductors have spurred the use of arylthioethers as intermediates for the synthesis of polyfulvalenes with extended conjugation [2]. Quite recently, *Cox et al.* have reported a novel photochromic tetraalkylthiobenzene [3].

Results from our laboratory have shown that tetraglyme *(2,5,8,11,14-pentaoxapentadecane)* is a suitable solvent for the substitution of unactivated halobenzenes by arene and alkanethiolate anions [4–7], which provides an alternative to *N,N*-dimethylacetamide [8], *N,N*-dimethylformamide [9], and the suspected carcinogen hexamethylphosphoric triamide (HMPT) [10]. In tetraglyme [6], limited mechanistic study suggested that a S_NAr mechanism [11] is operative in the substitution of unactivated halobenzenes by alkanethiolates. Similarly, the results of *Tiecco* and coworkers [10b] suggested that a S_NAr mechanism is operative in HMPT. The substitution of iodobenzenes with arenethiolate anions by a $S_{RN}1$ mechanism [12][2]) has been reported in the photostimulated reaction by *Bunnett* and *Creary* [13], whereas *Rossi* and coworkers [14] reported the competition between electron transfer (ET) and fragmentation of the radial anion intermediate of analogous $S_{RN}1$ reactions with thiolate anions.

The substitution of naphthyl and anthryl halides by thiolate anions has received considerably less attention [15], although evidence for an $S_{RN}1$ mechanism under certain

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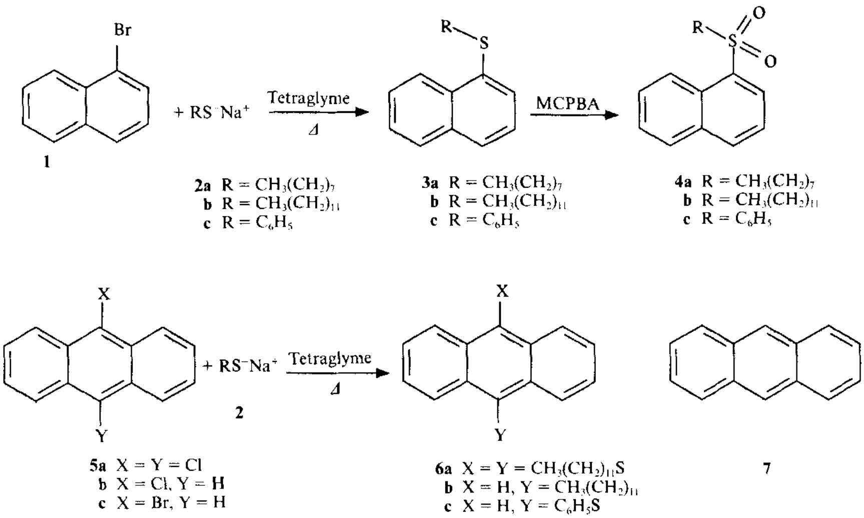
[2]) For a discussion of photostimulated $S_{RN}1$ reactions of aryl halides with thiolate anions, see [12b].

conditions has been presented [13] [14] [16]. The lower reduction potential [17] of polyarene systems suggests that single-electron-transfer (SET) processes might be facile. Quite recently, *Ashby et al.* have reported SET from lithium 1-butanethiolate to polynuclear hydrocarbons [18]. The counterion and solvent are known to effect the competition between ET and S_N2 mechanisms, and *Kuivila* and coworkers have demonstrated significant differences between tetraglyme and other solvents in the reaction of trimethylstannates and alkyl bromides [19]. In the present study, the results of the substitution of naphthyl and anthryl halides by both alkane- and arenethiolate anions in tetraglyme are reported.

Results and Discussion. – The reaction of the 1-bromonaphthalene (**1**) with the alkanethiolate anions **2a**–**b** in tetraglyme gave the corresponding 1-naphthyl thio-ethers **3a**–**b**, respectively *(Scheme 1)*. Similarly, the reaction of the benzenethiolate **2c** with **1** proceeded in the expected manner to give **3c**. Further proof of structure was provided by oxidation of **3a**–**c** with *m*-chloroperoxybenzoic acid [20] to the corresponding sulfones **4a**–**c**.

Scheme 1



The reaction of the dichloro-substituted anthracene **5a** with the alkanethiolate **2b** gave the bis(alkylthio)anthracene **6a** in high yield (95% recrystallized). The mono-substituted product **6b** was prepared in an analogous manner by the reaction of 9-bromoanthracene (**5c**) with the alkanethiolate **2b**.

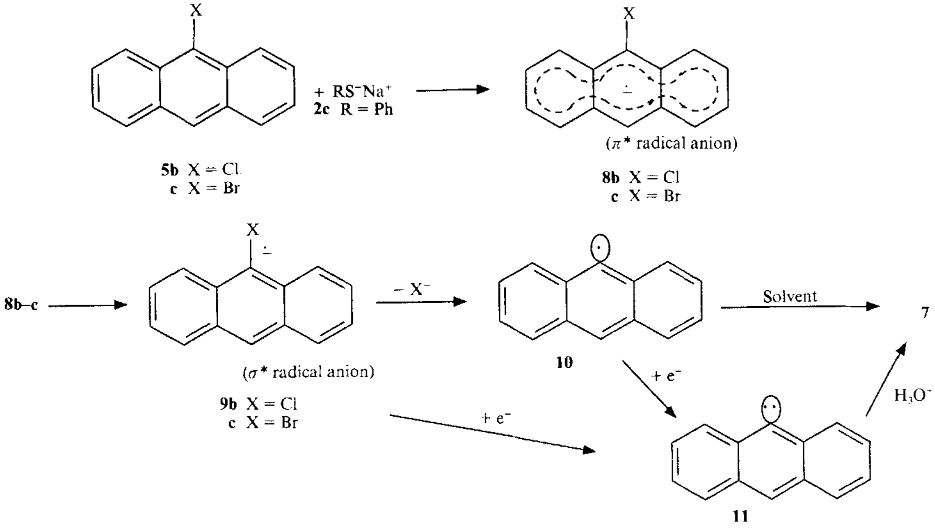
Surprisingly, the reaction of the benzenethiolate **2c** with **5c** gave a mixture of two major products. Upon recrystallization, a mixture of the two components was obtained with a m.p. range of 128–135° *(vide infra)*. The compounds could be separated by preparative TLC. One component was the expected 9-(phenylthio)anthracene (**6c**) which was identified by m.p., ^{1}H-NMR, MS, and elemental analysis. The other component was anthracene (**7**) which was identified by mixed m.p., MS, superimposable ^{1}H-NMR, and IR spectra with the spectra obtained from an authentic sample of **7**, and identical R_f on

TLC. The integration of the ^{1}H-NMR *singlet* resonances at δ 8.60 (H–C(10) of **6c**) and δ 8.40 (H–C(10) of **7**) indicated a 3:1 mixture **6c**/**7** prior to TLC separation.

Previously, *Beckwith et al.* reported the formation of a solid 'which could not be further purified' besides **6c** and Ph_2S in the reaction of anthracene with phenylthiyl radicals generated in benzene solution. The similarity of the m.p. range and elemental analysis of the mixture obtained in this study to that obtained by *Beckwith*, suggests that *Beckwith* isolated a similar mixture **6c**/**7** [21]3). Furthermore, the observation of anthracene in the present study suggested that a radical process may be operative.

The formation of **7** can be explained, if SET from the arenethiolate **2c** to **5c** occurred in competition with the expected S_NAr mechanism *(Scheme 2)*. The formation of both **7** and **6c** by an $S_{RN}1$ mechanism appears unlikely, because the formation of a σ radical **10** is required, which, by analogy to the highly reactive and unselective phenyl radical [22], would be expected to be rapidly reduced by H-atom extraction from the polyether solvent [22a] [23]4). In certain cases, mechanisms involving nucleophilic attack on a radical anion or the involvement of dianions have been proposed5). A reasonable explanation for the formation of **7** is that a SET process occurs which leads to the formation of **10** followed by H-atom extraction. The further reduction of the radical intermediate **10** to the anion **11**, which is protonated upon workup to give **7**, is also possible based upon the fact that the reduction of aryl radicals is generally easier than that of the starting substrate [23e]. Proton capture from monoglyme by an aryl anion has also been suggested [23a]. *Bunnett*

Scheme 2



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3) This study: m.p. 128–135°. Anal. found: C 85.3, H 5.3. [21]: m.p. 132.5–135°. Anal. found: C 86.6, H 5.2; calc. for a 3:1 mixture: C 86.5, H 5.1.

4) The formation of some **6c** either by radical coupling of **10** with **2c** or a $S_{RN}1$ process with a short chain length is of course possible. The rate constant for the reaction of a naphthyl radical, which would be expected to have similar reactivity to an anthryl radical, with **6c** ($k_2 = 2.3 \cdot 10^7 \text{M}^{-1}\text{l s}^{-1}$) is large [25d].

5) For a proposed mechanism involving nucleophilic attack on a radical anion, see [24a, b]. For a similarly proposed chain mechanism, see [24c]. For a review of radical anions and dianions generated from aromatic compounds, see [24d].

and coworkers have also demonstrated that an overall two-electron reduction process, whereby the initially formed radical anion is reduced directly to an aryl anion, is operative in certain cases [23b]. This mechanistic pathway proposed by *Bunnett* and coworkers, provides an alternate mechanism for the reduction of **5c** to **11**, which does not involve the σ radical **10**.

Given the posit that the formation of **7** occurs as the result of the formation of **10** (or **11**) through an ET mechanism *(Scheme 2)*, internal electron transfer from the initial π^* radical **8c** to the σ^* radical **9c** must occur prior to the cleavage of the C–X bond [23e] [25–28]. The Br or Cl substituent in **5b–c**, whose bonding orbital is orthogonal to the π system, does not have a significant effect on the reduction potential of the anthryl halide (E^0 values are -1.71 eV and -1.70 eV for **5b** and **5c**, respectively) [23e]. However, the σ^* orbital-energy level of the C–Br bond is lower than that of a C–Cl bond, and transfer of the electron from the π^* to the σ^* orbital (the intersection of the π^* and σ^* potential-energy surfaces) is expected to be more facile [23e] [28] [29]. This is consistent with both the observed cleavage rates of the radical anions **8b–c** ($\log k$ [s^{-1}] = 2.2 and 6.4, respectively) and the energy of activation calculated for their cleavage by extended *Hückel* calculations ($E^* = 25$ kcal · mol^{-1} and 16.5 kcal · mol^{-1}, respectively) reported by *Savéant et al.* [23e]. The straightforward substitution of **1** is consistent with the higher (more negative) reduction potential of the naphthalene ring system ($E^0 = -2.19$ eV for **1** [23e]) compared to the anthracene ring system.

As anticipated, the reaction of **5b** with **2c** gave the substitution product **6c** (59% recrystallized). The examination of the reaction mixture prior to workup by TLC did not reveal the presence of **7**. The observation of SET reactions in the case of the reaction of the **2c** but not the alkanethiolate has been previously observed in other studies *(vide infra)*, and is consistent with measured redox potentials of benzenethiolate ($E^0 = -0.2$ eV) *vs.* an alkanethiolate ($E^0 = 0.3$ eV for ethanethiolate) measured in MeCN [30].

The stability of **5c** under the reaction conditions was investigated. A solution of **5c** in tetraglyme was heated at both 125° for 12 h and 185° for 20 h. In neither case was the formation of **7** observed. Although the TLC of the solution **5c** heated at 185° showed no perceptible change, the solution became dark yellow and developed a distinct bromine-like odor.

Significantly, the formation of **7** was not observed when a 2:1 molar ratio of **2c**/**5c** in tetraglyme was stirred at 24° for 6 h. Quite interestingly, the slow formation of **6c** was observed when the same solution of **5c** and **2c** was heated at 103° for 7 days[6]) *without the formation of* **7**. These results strongly suggest that the SET process has a higher free energy of activation ($\Delta G^{\neq}$) and occurs as a result of the high temperatures employed in these substitutions (for a discussion, *cf.* [30b], pp. 23–25). The higher energy level of the C–Cl σ^* orbital in the case of **5b** precludes the formation of **7**.

A mixture of **6c** and **2c** in a 2:1 molar ratio in tetraglyme was heated at 50° (11 h) and 150° (48 h). In both cases, the formation of **7** was not observed, which suggests **6c** is not readily reduced under the reaction conditions.

A similar dichotomy between the reactivity of alkane- and benzenethiols was observed by *Takikawa et al.* in their reaction with 9-nitroanthracene [31]. The formation of

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[6]) Compound **6c** was isolated and identified by both ^{1}H-NMR and identical R_f on TLC with an authentic sample.

9-(alkylthio)anthracenes was observed in the substitution of 9-nitroanthracene with alkanethiols, whereas the reaction with benzenethiol gave a low yield of substitution products. Products which were the result of SET from benzenethiol to 9-nitroanthracene were reported. Similar observations were reported by *Singh* and *Jayaraman* for the reaction of 9-bromo-9-phenylfluorene with benzenethiolate anion [32].

Recently, *Handoo* and *Gadru* [33] reported that Zn/KOH (Zn/OH^-) in DMSO is a strong reductant, which can reduce organic substrates with a reduction potential of up to – 2.2 eV to their corresponding radical anions. The radical anions were reported to form readily 'even in the absence of inert conditions' unlike the corresponding reactions in etheral solvents which are quite sensitive to atmospheric O_2. The similar high-dielectric constant and solvating ability suggested that radical anions might also be readily formed in tetraglyme. Indeed, **5b–c** and **6c** were readily reduced by Zn/OH^- in tetraglyme in moderate to high yield. The reaction mixtures quickly developed a violet-to-intense-blue-black coloration, suggestive of radical-anion intermediates.

The results of this study demonstrate that SET processes can occur in competition with substitution in the reaction of readily reduced haloarenes by benzenethiolate anion, particularly when the σ^* orbital of the C—nucleofuge bond is low enough in energy to accept an electron from the π^* radical. This work further suggests that in the synthesis of arylthioarenes the occurrence of SET reactions can be obviated by the use of nucleofugal groups that form bonds to the arene with a high σ^* orbital energy.

Experimental Part

General. Reagents were purchased from commercial laboratory supply houses. Tetraglyme was dried prior to use by passing through an activated column of alumina (*Woelm N*). Reactions were carried out in flame-dried apparatus under a dry, inert atmosphere of either N_2 or Ar.

Whatmann DSC-1F silica gel was used for all dry-column chromatography [34]. *Merck 9385* silica gel *60* (230–400 mesh) was used for flash chromatography [35]. *Merck* pre-coated (0.25 mm) silica gel *60 F-254* plates were used for TLC. *Merck* pre-coated (2 mm) silica gel *60 F-254* plates were used for prep. TLC. Prep. HPLC was carried out with a *Waters PREP 500A HPLC*.

All m.p. were determined in open capillary tubes with a *Thomas-Hoover* apparatus and are uncorrected. IR spectra were recorded on a *Perkin-Elmer* model *1300* spectrophotometer, and reported peak absorptions are estimated to be accurate to ± 10 cm^{-1}. ^{1}H-NMR spectra were taken on a *Jeol FX-90Q*, *Varian* model *CFT-20*, or

Table. *Reactions of Haloarenes with Sodium Thiolates in Tetraglyme*

Entry	Substrate	R in RSNa	mol-equiv. RSNa	Reaction temp. [°C]	Reaction time [h]	Product	Yield[a]) [%]
1	1-Br-naphthalene	1-octyl	1.1	175	20	**3a**	67[b])
2	1-Br-naphthalene	1-dodecyl	1.1	175	22	**3b**	81[b])
3	1-Br-naphthalene	Ph	1.1	163	23	**3c**	62[b])
4	9,10-Cl_2-anthracene	1-dodecyl	2.2	169	23	**6a**	95
5	9-Br-anthracene	1-dodecyl	1.1	181	22	**6b**	42[c])
6	9-Br-anthracene	Ph	1.1	195	16	[d])	–
7	9-Cl-anthracene	Ph	1.1	183	12	**6c**	59

[a]) Isolated yield (recrystallized). [b]) Isolated by distillation. [c]) Isolated by dry-column chromatography.
[d]) A mixture of anthracene and **6c** obtained.

Varian model *XL-200* spectrometer. All ^1H chemical shifts are reported in ppm relative to TMS. MS were obtained on a *Finnegan* model *8200* mass spectrometer.

Elemental analyses were performed by *Analytical Research Services, Ciba-Geigy Corp.*

The preparation of **3a** is illustrative of the general method for the preparation of compounds **3b–c** and **6a–b**. The molar equivalents of thiol, reaction temperature, reaction duration, and yields are listed in the *Table*.

1-(1-Octylthio)naphthalene (**3a**). To a well-stirred mixture of 2.64 g (110 mmol) of NaH and 50 ml of tetraglyme was added dropwise (exotherm) a soln. of 16.09 g (110 mmol) of 1-octanethiol in 150 ml of tetraglyme. After the evolution of H_2 was complete (*ca.* 1 h), 20.71 g (100 mmol) of **1** was added, and the resultant mixture was heated at 175° for 20 h. The cooled mixture was added to 500 ml of dil. aq. HCl, and the resultant heterogeneous mixture was extracted with Et_2O (1 × 500 ml). The org. phase was separated and was extracted with H_2O (3 × 165 ml). The org. phase was dried (Na_2SO_4), and the volatiles were removed *in vacuo*. The residue was purified by bulb-to-bulb and fractional distillation to give 24.40 g (67%) of a light yellow liquid. B.p. 150°/0.01 Torr; R_f (7:3 hexane/AcOEt) 0.66. ^1H-NMR ($CDCl_3$): 0.89 (*t*, 3 H); 1.27–1.58 (complex *m*, 12 H); 2.96 (*t*, SCH_2); 7.58 (complex *m*, 6 H); 8.46 (complex *m*, 1 H). Anal. calc. for $C_{18}H_{24}S$: C 79.4, H 8.9; found: C 79.5, H 9.1.

1-(1-Dodecylthio)naphthalene (**3b**). Light yellow liquid, b.p. 192–195°/0.15Torr ([41]: 195–196°/0.01 Torr); R_f (7:3 heptane/AcOET) 0.46. ^1H-NMR ($CDCl_3$): 1.02 (*t*, 3 H); 1.40 (complex *m*, 20 H); 3.08 (*t*, SCH_2); 7.65 (complex *m*, 6 H); 8.56 (complex *m*, 1 H). Anal. calc. for $C_{22}H_{32}S$: C 80.4, H 9.8; found: C 80.2, H 10.1.

1-(Phenylthio)naphthalene (**3c**). White solid; purified by distillation (143–147°/0.1 Torr) followed by recrystallization from EtOH. M.p. 42–43.5° ([36]: 41–42°; [37]: 41.5–42°; [38]: 41.8°; [39]: 39.0–49.5°); R_f (7:3 heptane/AcOEt) 0.46. ^1H-NMR ($CDCl_3$): 7.33–8.05 (complex *m*, 11 H); 8.61 (complex *m*, 1 H). Anal. calc. for $C_{16}H_{12}S$: C 81.3, H 5.1; found: C 81.2, H 5.3.

9,10-Bis(1-dodecylthio)anthracene (**6a**). White solid; purified by recrystallization from acetone. M.p. 67.5–69.5°. R_f (7:30 heptane/AcOEt) 0.76. ^1H-NMR ($CDCl_3$): 0.89 (*t*, 6 H); 1.27 (complex *m*, 40 H); 2.90 (*t*, 2 SCH_2); 7.65 (*m*, 4 H); 9.08 (*m*, 4 H). Anal. calc. for $C_{38}H_{58}S_2$: C 78.8, H 10.1; found: C 78.9, H 10.0.

9-(1-Dodecyl)anthracene (**6b**). White solid[7]; purified by dry-column chromatography (9:1 heptane/AcOEt). R_f (heptane) 0.15. ^1H-NMR ($CDCl_3$): 0.96 (*t*, 3 H); 1.33 (complex *m*, 20 H); 2.90 (*t*, SCH_2); 7.58 (complex *m*, 4 H); 8.02 (*dd*, 2 H); 8.46 (*s*, 1 H); 9.05 (*dd*, 2 H). Anal. calc. for $C_{26}H_{34}S$: C 82.5, H 9.1; found: C 82.2, H 9.4.

9-(Phenylthio)anthracene (**6c**). White crystalline solid, purified by recrystallization from i-PrOH. M.p. 98–100° ([21]: 100.5–102°). R_f (heptane) 0.17. ^1H-NMR ($CDCl_3$): 7.00 (complex *m*, 5 H); 7.52 (complex *m*, 4 H); 8.10 (complex *m*, 2 H); 8.60 (complex *m*, 1 H); 8.84 (complex *m*, 2 H). MS: 286 (M^+). Anal. calc. for $C_{20}H_{14}S$: C 83.9, H 4.9; found: C 83.9, H 4.9.

1-Octyl 1-Naphthyl Sulfone (**4a**). To a soln. of 2.72 g (10 mmol) of **3a** in 40 ml of CH_2Cl_2 cooled with an acetone/ice bath was added portionwise with a powder-addition funnel 3.80 g (22 mmol) of *m*-chloroperoxybenzoic acid. The resultant mixture was stirred for two hours at r.t. and then was extracted sequentially with a 10% aq. soln. of Na_2SO_3, sat. aq. $NaHCO_3$ soln., and H_2O. The org. phase was dried (Na_2SO_4), and the volatiles were removed *in vacuo*. The residue was purified by dry-column chromatography (heptane) to give 2.50 g (82%) of a light amber viscous liquid, R_f (7:3 heptane/AcOEt) 0.36. IR (CH_2Cl_2): 1305, 1152, 1122 (SO_2). ^1H-NMR ($CDCl_3$): 0.77 (*t*, 3 H); 1.08–1.65 (complex *m*, 12 H); 3.27 (*t*, 2 H); 7.58–8.27 (complex *m*, 6 H); 8.71 (complex *m*, 1 H). Anal. calc. for $C_{18}H_{24}O_2S$: C 71.0, H 8.0; found: C 71.0, H 8.1.

1-Dodecyl 1-Naphthyl Sulfone (**4b**). By the procedure used to prepare **4a**, compound **4b** was prepared from 3.29 g (10 mmol) of **3b** and 3.80 g (22 mmol) of *m*-chloroperoxybenzoic acid. The residue was recrystallized from EtOH to give 2.57 g (71%) of a light-beige solid. M.p. 29–31°. R_f (7:3 heptane/AcOET) 0.37. IR (CH_2Cl_2): 1300, 1153, 1122 (SO_2). ^1H-NMR ($CDCl_3$): 0.90 (*t*, 3 H); 1.21–1.83 (complex *m*, 20 H); 3.33 (*t*, 2 H); 7.71–8.33 (complex *m*, 6 H); 8.77 (complex *m*, 1 H). Anal. calc. for $C_{22}H_{32}O_2S$: C 73.3, H 9.0; found: C 72.9, H 8.9.

1-Phenyl 1-Naphthyl Sulfone (**4c**). By the procedure used to prepare **4a**, compound **4c** was prepared from 2.36 g (10 mmol) of **3c** and 3.80 g (22 mmol) of *m*-chloroperoxybenzoic acid. The residue was recrystallized from EtOH to give 1.15 g (43%) of a white solid. M.p. 102–103° ([15]: 99.5–100.5°). *Rf* (7:3 heptane/AcOEt) 0.20. IR (CH_2Cl_2): 1305, 1155, 1135 (SO_2). ^1H-NMR ($CDCl_3$): 7.46 (complex *m*, 6 H); 7.96 (complex *m*, 4 H); 8.58 (complex *m*, 2 H). Anal. calc. for $C_{16}H_{12}SO_2$: C 71.6, H 4.5; found: C 72.0, H 4.7.

General Procedure for Zn/KOH Reductions in Tetraglyme. To a mixture of 1 mmol of substrate and 0.5 g (7.6 mmol) of Zn dust in 20 ml of tetraglyme was added 3 ml of an aq. 6 M KOH soln. The mixture was heated to 55° and then allowed to cool to r.t. The reaction mixture was stirred at r.t. overnight, and then it was poured into 125 ml of Et_2O. The ethereal solution was extracted with sat. NaCl soln. (3 × 50 ml), and the org. phase was dried (Na_2SO_4).

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[7] A white crystalline solid is obtained from cold i-PrOH which liquifies upon warming to r.t.

The volatiles were removed *in vacuo*, and the residue was purified by recrystallization. The following yields of **7**[8] were obtained:

Substrate	Yield **7** [%]
5b[9]	79
5c[9]	45
6c[10]	90

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REFERENCES

[1] a) D.D. MacNicol, D.R. Wilson, *Chem. Ind (London)* **1977,** 85; b) A.D.U. Hardy, D.D. MacNicol, D.R. Wilson, *J. Chem. Soc., Perkin Trans. 2* **1979,** 1101; c) D.D. MacNicol, P.R. Mallison, C.D. Robertson, *J. Chem. Soc., Chem. Commun.* **1985,** *23,* 1649.

[2] a) P. Wolf, K. Müllen, M. Przybylski, *Chimia* **1986,** *40,* 200; b) For a related study, see: H. Miyamoto, K. Yui, Y. Aso, T. Otsubo, F. Ogura, *Tetrahedron Lett.* **1986,** *27,* 2011; c) K. Yui, Y. Aso, T. Otsubo, F. Ogura, *Chem. Lett.* **1986,** 551.

[3] S.D. Cox, C.W. Dirk, F. Moras, D.E. Wellman, F. Wudl, M. Soltis, C. Strouse, *J. Am. Chem. Soc.* **1984,** *106,* 7131.

[4] S.D. Pastor, J.D. Spivack, D.W. Hughes, *Sulfur Lett.* **1984,** *2,* 71.

[5] S.D. Pastor, J.D. Spivack, D.W. Hughes, *Phosphorus Sulfur* **1984,** *21,* 39.

[6] S.D. Pastor, E.T. Hessell, *J. Org. Chem.* **1985,** *50,* 4812.

[7] S.D. Pastor, H.K. Naraine, R. Sundar, *Phosphorus Sulfur* **1988,** in press.

[8] P.A. Odorisio, S.D. Pastor, J.D. Spivack, *Phosphorus Sulfur* **1982,** *12,* 309.

[9] L. Testaferri, M. Tiecco, M. Tingoli, D. Chianelli, M. Montanucci, *Synthesis* **1983,** 751.

[10] a) P. Cogolli, L. Testaferri, M. Tingoli, M. Tiecco, *J. Org. Chem.* **1979,** *44,* 2636; b) P. Cogolli, F. Maiolo, L. Testaferri, M. Tingoli, M. Tiecco, *J. Org. Chem.* **1979,** *44,* 2642; c) L. Testaferri, M. Tingoli, M. Tiecco, *Tetrahedron Lett.* **1980,** *21,* 3099; d) L. Testaferri, M. Tingoli, M. Tiecco, *J. Org. Chem.* **1980,** *45,* 4376.

[11] J. March, 'Advanced Organic Chemistry', 3rd. edn., John Wiley & Sons, New York, 1985, pp. 576–578.

[12] a) Z.V. Todres, *Phosphorus Sulfur* **1981,** *9,* 353; b) For a discussion of photostimulated $S_{RN}1$ reactions of aryl halides with thiolate anions, see: R.A. Rossi, R.H. de Rossi, 'Aromatic Substitution by the $S_{RN}1$ Mechanism', American Chemical Society, Washington, DC, 1983, pp. 218–224.

[13] J.F. Bunnett, X. Creary, *J. Org. Chem.* **1974,** *39,* 3173.

[14] a) R.A. Rossi, R.H. de Rossi, A.F. Lopez, *J. Am. Chem. Soc.* **1976,** *98,* 1252; b) R.A. Rossi, S.M. Palacios, *J. Org. Chem.* **1981,** *46,* 5300; c) A.B. Pierini, M.T. Baumgartner, R.A. Rossi, *ibid.* **1987,** *52,* 1089.

[15] a) F. Krafft, E. Bourgeois, *Chem. Ber.* **1890,** *23,* 3045; b) A. Zweig, A.H. Maurer, B.G. Roberts, *J. Org. Chem.* **1967,** *32,* 1322; c) J.S. Bradshaw, E.Y. Chen, R.H. Hales, J.A. South, *ibid.* **1972,** *37,* 2051; d) J.S. Bradshaw, J.A. South, R.H. Hales, *ibid.* **1972,** *37,* 2381; e) W.H. Pirkle, J.M. Finn, *ibid.* **1983,** *48,* 2779; f) W. Poules, K. Praefcke, *Chem.-Ztg.* **1983,** *107,* 373.

[16] a) J.A. Zeitewicz, T.M. Oestreich, *J. Am. Chem. Soc.* **1973,** *95,* 6863; b) For a related study, see: A.B. Pierini, R.A. Rossi, *J. Org. Chem.* **1979,** *44,* 4667; c) R. Beugelmans, H. Ginsburg, *Tetrahedron Lett.* **1987,** *28,* 413.

[17] C.K. Mann, K.K. Bannes, 'Electrochemical Reactions in Nonaqueous Systems', Marcel Dekker, New York, 1970.

[18] E.C. Ashby, W.S. Park, A.B. Goel, W.-Y. Su, *J. Org. Chem.* **1985,** *50,* 5184.

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[8] Anthracene was identified by m.p., TLC, and both the IR and ^{1}H-NMR spectra were superimposable with the spectra of an authentic sample.

[9] The reaction mixture was a light-purple color throughout.

[10] The reaction mixture became intense blue-black in color and slowly faded to a yellow-orange color after stirring for one hour.

[19] a) H.G. Kuivila, W.G. Reeves, *Bull. Soc. Chim. Belg.* **1980,** *89,* 801; b) M.S. Alnajjar, H.G. Kuivila, *J. Am. Chem. Soc.* **1985,** *107,* 416.

[20] J.J. Rigau, C.C. Bacon, C.R. Johnson, *J. Org. Chem.* **1970,** *35,* 3655 and ref. cit. therein.

[21] a) A.L.A. Beckwith, B.S. Low, *J. Chem. Soc.* **1961,** 1304; b) A.L.J. Beckwith, B.S. Low, *J. Chem. Soc.* **1964,** 2571.

[22] a) R.F. Bridger, G.R. Russell, *J. Am. Chem. Soc.* **1963,** *85,* 3754; b) A. Clerici, F. Minisci, O. Porta, *Gazz. Chim. Ital.* **1973,** *103,* 171; c) K.U. Ingold, in: J.K. Kochi (Ed.), 'Free Radicals', Wiley, New York, 1973, Vol. I, pp. 70–83 and ref. cit. therein; d) T. Suehiro, A. Suzuki, Y. Tsuchida, J. Yamazaki, *Bull. Chem. Soc. Jpn.* **1977,** *50,* 3324; e) C. Wentrup, 'Reactive Molecules', Wiley, New York, 1984, pp. 82–83.

[23] a) J.F. Garst, *Acc. Chem. Res.* **1971,** *4,* 400; b) R.A. Rossi, J.F. Bunnett, *J. Am. Chem. Soc.* **1974,** *96,* 112; c) C. Amatore, J. Chaussard, J. Pinson, J.-M. Savéant, A. Thiébault, *ibid.* **1979,** *101,* 6012; d) C. Amatore, J. Pinson, J.-M. Savéant, A. Thiébault, *ibid.* **1981,** *103,* 6930; e) C.P. Andrieux, J.M. Savéant, D. Zann, *Nouv. J. Chim.* **1984,** *8,* 107.

[24] a) T. Abe, Y. Ikegami, *Bull. Chem. Soc. Jpn.* **1976,** *49,* 3227; b) T. Abe, Y. Ikegami, *ibid.* **1978,** *51,* 196–200; c) G.L. Russell, B. Mudryk, F. Ros, M. Jawdosiuk, *Tetrahedron* **1982,** *38,* 1059–1067; d) For a review of radical anions and dianions generated from aromatic compounds, see N.L. Holy, *Chem. Rev.* **1974,** *74,* 243.

[25] K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura, C. Nagata, *Bull. Chem. Soc. Jpn.* **1962,** *35,* 38.

[26] a) R.A. Rossi, S.M. Palacios, *J. Org. Chem.* **1981,** *46,* 5300–5304; b) R.A. Rossi, *Acc. Chem. Res.* **1982,** *15,* 164–170; c) R.A. Rossi, *J. Chem. Educ.* **1982,** *59,* 310–312.

[27] F.A. Beland, S.O. Farwell, P.R. Calles, R.D. Geer, *J. Electroanal. Chem. Interfacial Electrochem.* **1977,** *78,* 145.

[28] J.K. Kochi, 'Organometallic Mechanism and Catalysis', Academic, New York, p. 171 and ref. cit. therein.

[29] H. Riederer, J. Hüttermann, *J. Chem. Soc., Chem. Commun.* **1978,** 313.

[30] a) L. Erbsen, *Acta Chem. Scand. Ser. B* **1984,** *38,* 439; b) L. Eberson, 'Electron Transfer in Organic Chemistry', Springer-Verlag, Berlin, 1987, p. 62.

[31] Y. Takikawa, T. Abe, R. Sato, Takizawa, *Chem. Lett.* **1980,** 25.

[32] P.R. Singh, B. Jayaraman, *Indian J. Chem.* **1974,** *12,* 1306.

[33] K.L. Handoo, K. Gadru, *Tetrahedron Lett.* **1986,** *27,* 1371.

[34] B. Loev, M.M. Goodman, *Chem. Ind. (London)* **1967,** 2026.

[35] C.W. Still, M. Kahn, J. Mitra, *J. Org. Chem.* **1978,** *43,* 2923.

[36] H. Seeboth, *Monatsber. Deut. Akad. Wiss. (Berlin)* **1967,** *9,* 108.

[37] J. Nakayama, T. Fujita, M. Hoshino, *Chem. Lett.* **1983,** 249.

[38] E. Bourgeois, *Chem. Ber.* **1985,** *28,* 2312–2331.

[39] A.H. Weinstein, R.M. Pierson, *J. Org. Chem.* **1958,** *23,* 544.