36. The Reaction of 9-Bromoanthracene with Benzenethiolate Anion in Tetraglyme: Evidence against a Competing Electron-Transfer Mechanism

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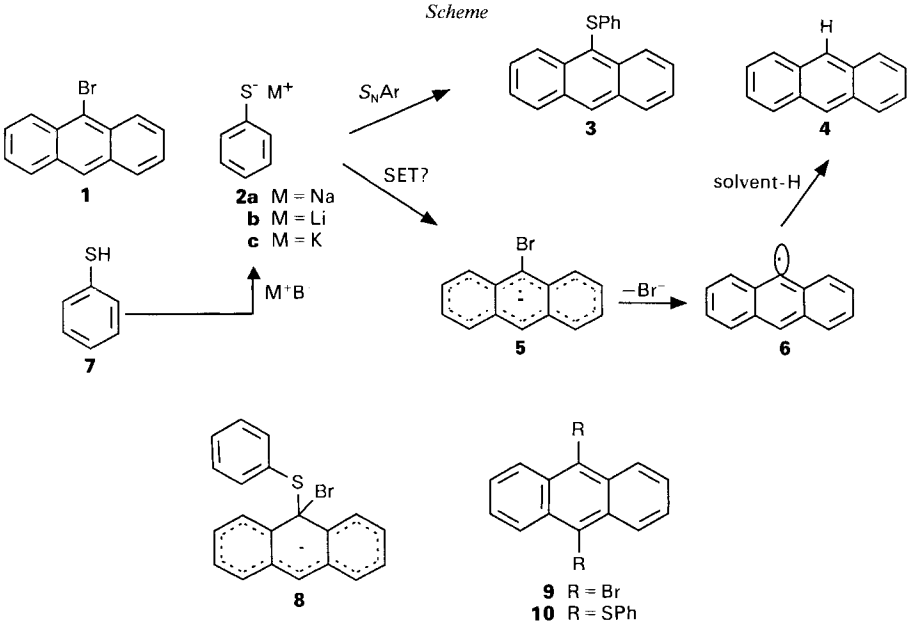
(8.I.92)

The reaction of 9-bromoanthracene (**1**) with benzenethiol(ate) in tetraglyme proceeds by a S_NAr mechanism. The concurrent formation of anthracene is not due to a competing single-electron-transfer pathway involving either benzenethiol or benzenethiolate anion.

The involvement of single-electron-transfer (SET) pathways in organic chemistry is a topic of fundamental importance (for reviews, see [1]). The occurrence of chain mechanisms involving radical anions for the substitution of both alkyl and aryl halides, the $S_{RN}1$ mechanism, was delineated [2]. Quite recently, however, a mechanistic reappraisal of the involvement of aryl σ radicals in the $S_{RN}1$ substitution of aryl halides appeared [3a] (for references to the $S_{RN}2$ mechanism, see [3b]).

The substitution of 9-bromoanthracene (**1**) with sodium benzenethiolate (**2a**) in the solvent tetraglyme (= 2,5,8,11,14-pentaoxapentadecane) gave, besides te expected substitution product 9-(phenylthio)anthracene (**3**), the reduction product anthracene (**4**) [4] [5] (see *Scheme*). It was reasonably suggested that the formation of **4** was the result of a SET

Scheme



from **2a** to **1** that resulted initially in the formation of the radical anion **5** with subsequent loss of bromide to give the anthryl σ radical **6**. H-Atom abstraction by **6** from the polyether solvent provides a plausible mechanistic pathway for the formation of **4**. Indeed, anthracene was used as trap for radical anions in mechanistic studies investigating the involvement of SET processes [6]. *Takikawa et al.* demonstrated that a SET process was involved in the reaction of benzenethiol (**7**) with 9-nitroanthracene [7]. Similar conclusions were made by *Singh* and *Jayaraman* for the mechanism of the reaction of 9-bromo-9-phenylfluorene with benzenethiolate anion [8]. A competition between S_NAr and SET mechanisms in the reaction of **1** with **2a** was proposed. In this paper, evidence is presented that SET from **2a** is *not* involved and the formation of **4** is the result of an independent mechanism.

Results and Discussion. – The products of the reaction of **1** with various benzenethiolate salts, which were prepared *in situ* from **7** and the appropriate base, under an inert atmosphere of N_2 were monitored by GLC analysis as a function of time. The analytical results at selected time intervals are given in the *Table*. The time equal zero sample (t_0) was taken when the reaction temperature reached 145°. The reagent grade **1** used was found to contain 1.3 ± 0.1 mol-% of **4**. The thermal stability of **1** at 150° in tetraglyme was monitored as a function of time to verify that **4** was not formed by a thermal process. The 9-bromoanthracene (**1**) was observed to be thermally stable, and the formation of **4** was not observed (*Entry 1*). The aliquotes of reaction mixture sampled were found to contain the same mol-% of **1** and **4** within experimental error (standard deviation = ± 0.1 mol-%) as the starting material. Furthermore, this experiment verifies that impurities in the solvent did not result in the formation of **4**.

In the reaction of **1** with **2a**, which was prepared from **7** and NaH, the formation of **4** was observed (*Entry 2*). The mol-% of **4** observed increased during the first h of the reaction from 0.4 at t_0 to the final value of 1.1 at t_{120}. The mol-% of **3** increased from 11.9 at t_0 to 66.3 at t_{120} during this same time interval. The identical reaction run at double the concentration of reactants lead to the same mol-% of **4** at t_{120} (1.0 ± 0.1 %), whereas the rate of formation of **3** increased (*Entry 3*). Again the formation of **4** occurred rapidly during the first h of the reaction to a constant level. The increase in reaction rate with a higher concentration of reactants is consistent with a S_NAr mechanism. The observation of the rapid initial formation of **4** further suggests that **4** is produced by a mechanism independent of the formation of **3**.

The rapid formation of **4** during the first 15 min suggests that a complex consisting of unreacted NaH, **7**, and **2a** may be responsible for the reaction to **4**. Complex reducing agents prepared from NaH and alcohols are known to reduce both alkyl and aryl halides [9a–c][1]). Not unexpectedly, the reaction of NaH alone with **1** led to the formation of 5.5 mol-% of **4** at t_{60} (*Entry 4*). The reaction of 2 equiv. of NaH with 1 equiv. of both **1** and **7** led to 4.1 mol-% of **4**, 95.0 mol-% of **3**, and 0.9 mol-% of unreacted **1** at t_{120} (*Entry 5*). The reaction mixture contained 95.8 mol-% of **3** and 1.6 mol-% of **1** at t_{45}, *i.e.*, a higher concentration of substitution product **3** at t_{45} than at t_{120}. This observation suggests that a slow process leading to the reduction of **3** to **4** is operative (*vide infra*).

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[1]) For the direct reduction of α-haloketones with thiols, see [9d]; for a recent study, see [9e].

Table. *Product Compositions of the Reactions of 1 with Benzenethiol(ate) at Selected Times*[a])

Entry	Starting materials [mol-equiv.]			Base	Time	Products [mol-%][b])		
	1	**7**	base			**4**	**1**	**3**
1	1	–	–	–	120	0	100	–
2	1	1	1	NaH	0	0.4	87.7	11.9
					45	1.3	52.7	45.9
					120	1.1	32.6	66.3
3[c])	1	1	1	NaH	0	0	78.6	21.4
					30	0.6	19.3	80.1
					60	1.0	14.3	84.7
					120	1.0	10.4	88.7
4	1	–	1	NaH	0	0.6	99.4	–
					60	5.5	94.5	–
5	1	1	2	NaH	0	0	79.4	20.6
					15	1.7	7.7	90.6
					30	2.2	3.2	94.6
					45	2.6	1.6	95.8
					60	3.0	1.4	95.5
					120	4.1	0.9	95.0
6	1	10	1	NaH	0	0	0.6	99.4
					60	0	0	100
7	1	1	1	LiH	0	0	97.3	2.7
					120	1.1	47.8	51.1
8	1	1	1	$NaNH_2$	0	0	93.3	6.7
					120	0.9	36.8	62.3
9	1	1	1	*t*-BuOK	0	0	79.3	20.7
					30	0.6	10.3	89.1
					60	1.3	7.6	91.1
					120	1.6	4.1	94.3
10	1	2	2	*t*-BuOK	0	0	65.4	34.6
					120	0.8	0	99.2
11[d])	1	–	1	*t*-BuOK	30	5.9	94.2	–
					120	9.1[e])	90.1	–
12	1	1	–	–	0	0	44.0	56.0
					60	0	11.2	88.8
					120	0	8.7	91.3
13	1	2	–	–	660	0	1.3	98.7

[a]) Reaction temperature 150 ± 3°. [b]) Standard deviations for mol-% of **4** is $\sigma \pm 0.1$ unless otherwise stated. Maximum $\sigma \pm 0.6$ for **1** and **3**. [c]) Reactant concentration doubled. [d]) Reaction temperature 25°. [e]) $\sigma \pm 0.6$ mol-%.

The reaction of **1** with **2a** was also carried out in the presence of a 10 molar excess of **7**: The formation of **3** was observed without that of **4** (*Entry 6*). The absence of **4** strongly suggests that SET from **2a** to **1** is not involved. Furthermore, the absence of increased levels of **4** provides evidence against the involvement of an anthryl σ radical **6**. This must be the case because **7** is a powerful H-atom donor and would be expected to rapidly donate a H-atom to **6**. The rate constants for H-atom abstraction from benzenethiol by various alkyl radicals [10] are all near $1.3 \cdot 10^8$. The 10 molar excess of **7** would also be expected to minimize the presence of any unreacted NaH complexed with either **7** or **2a** in the early stages of the reaction and is consistent with the observed lack of formation of **4** in the early stages of the reaction (*vide supra*).

To test this contention further, the reaction of **1** with lithium thiolate **2b** was examined: again the formation of 1.1 mol-% of **4** was observed (*Entry 7*). Evidence that the formation of **4**, however, was not necessarily the result of a simple hydride reduction of **1** was provided by the reaction of **1** with **2a** prepared *in situ* from **7** and $NaNH_2$ rather than with NaH (*Entry 8*). Essentially identical amounts of both **3** and **4** were found at t_{120} in the reaction using either NaH or $NaNH_2$ (compare *Entries 2* and *8*). The reaction of **1** with 1 equiv. of potassium thiolate **2c**, prepared *in situ* from **7** and *t*-BuOK, yielded 94.3 ± 0.2 mol-% of **3**, 1.6 ± 0.1 mol-% of **4**, and 4.1 ± 0.1 mol-% of unreacted **1** at t_{120} (*Entry 9*). The reaction of **1** with 2 equiv. of **2c** prepared from **7** and *t*-BuOK led to a somewhat lower level of **4**, whereas the more rapid formation of **3** with higher thiolate concentration is consistent with a bimolecular S_NAr mechanism (*Entry 10*). Interestingly, the formation of **4** in these reactions proceeded slowly over the course of the reaction when *t*-BuOK was used rather than a metal hydride as a base (compare *Entries 9* and *2*). The formation of **4** may be mechanistically different in these cases.

The stability of **1** in the presence of the relatively non-nucleophilic base *t*-BuOK was evaluated. Surprisingly, stirring a mixture of **1** with 1 equiv. of *t*-BuOK *at room temperature* led to the formation of 9.1 ± 0.6 mol-% of **4** at t_{120} (*Entry 11*); the reaction mixture developed a deep purple-blue coloration. At 150°, extensive formation of **4** at t_0 was obtained (47.3%), along with unreacted **1** (20.3%) and seven unidentified peaks in the GLC of the reaction mixture.

Several reports in the literature describe metalations using metal hydroxides, alkoxides, and amides [11] (for selected reviews and papers, see [12]). One possible mechanism for the formation of **4** would be metalation of **1** by *t*-BuOK followed by protonation during workup [13] [14][2]). To evaluate this possibility, samples of the reaction mixture were quenched with D_2O. D-Incorporation into the anthracene would be expected if metalation of **1** occurred. But GC-MS analysis of the reaction mixture revealed that the **4** formed contained no deuterium. Although this finding is consistent with a free-radical mechanism (formation of a radical anion by SET followed by fragmentation)[3]) involving abstraction of a H-atom by **6** from the solvent, more complex mechanisms involving both the metalation of tetraglyme and transfer of a proton to the 9-anthryl anion from tetraglyme prior to workup of the reaction mixture cannot be excluded. Indeed, the observed dehalogenation of 1,2,4-tribromobenzene with *t*-BuOK in dimethyl sulfoxide occurs by metalation that involves proton transfer from the solvent [16a][4]). The reductive hydrodehalogenation of 4-bromoisoquinoline with NaOMe and 8-chloro-3-ethylquinoline with KOH/poly(ethyleneglycol) was reported, although mechanistic information was not forthcoming [17]. The hydrodehalogenation of 2-bromonitrobenzene was shown to proceed by a mechanism involving a radical anion [18].

The formation of 0.3 mol-% of **4** was observed at t_{60}, after stirring a mixture of the product diaryl sulfide **3** with *t*-BuOK in tetraglyme at room temperature. At 150°, the slow formation of **4** was observed (0.9 mol-% at t_0 and 5.2 mol-% at t_{30}), along with other unidentified products. The more rapid reaction of **1** compared to **3** with *t*-BuOK suggests that the reduction of **1** is the likely source of **4**. The reaction of **1** with excess **2c** (see, *e.g.*,

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[2]) For metalation using complexes of *t*-BuOK and BuLi, see [13]; for numerous examples, see [14].

[3]) For the role of single-electron transfer in metal-halogen exchange, see [15a]; for ionic mechanisms, see [15b].

[4]) For references to the mechanism of the 'halogen dance', see [16b–f].

Entry 10) confirms an earlier report that **3** is stable towards excess benzenethiolate anion during the time interval studied [4]. Further work is needed to delineate the mechanism of the reduction of **1** to **4** by *t*-BuOK.

Recently, the direct high-temperature substitution of **1** by **7** in the absence of base either neat or in 2,4-dichlorotoluene was reported. The reaction was carried out in the presence of atmospheric oxygen. At 130°, a 53.9% yield of **3** and 27.0% yield of **4** were reported (based upon conversion of **1**), whereas at 180°, exclusive formation of **4** was observed (72%). A free-radical mechanism was postulated by the authors [19].

The reaction of **1** with 1 equiv. of **7** in tetraglyme *under a N_2 atmosphere* in the absence of base led to a mixture of 91.3 ± 0.2 mol-% of **3** and 8.7 ± 0.2 mol-% of **1** (*Entry 12*). The formation of **4** was not observed. Similarly, the reaction of **1** with 2 equiv. of **7** gave 98.7 mol-% of **3** without the formation of **4** (*Entry 13*). These observations demonstrate that **4** is not the result of reduction of **1** by **7**. Furthermore, the absence of **4** strongly suggests that the σ radical **6** is not involved in the formation of **3** (*vide supra*). The observation of the formation of **3** by the reaction of **1** with **7** in the absence of base is no doubt related to the ease of formation of the resonance-stabilized σ complex **8**, which is an intermediate in the S_NAr mechanism (for a discussion of the S_NAr mechanism, see [20]).

The present mechanistic results suggest that in the substitution of halogenoanthracenes with benzenethiolate, reduction products from the bromoanthracene can be minimized or eliminated by either using an excess of thiolate anion prepared from *t*-BuOK to minimize the competing reduction process(es) or using the thiol in the absence of base. The reaction of **1** with either 2 equiv. of **2c** or **7** gave the substitution product **3** in 60 and 77% recrystallized yield, respectively. Similarly, the reaction of **9** with either 2 equiv. of **2c** or **7** gave **10** in 86 and 76% recrystallized yield, respectively.

In conclusion, the results of this study are fully in accord with an S_NAr mechanism for the formation of **3** by the reaction of **1** with **2a–c**. This result is consistent with our previous mechanistic work in tetraglyme [5c] and the work of others [21] in dipolar aprotic solvents. The formation of the reduced product **4** is *not* the result of a competing SET process from either **2a–c** or **7**. The reduced product is formed by a competing mechanism(s) that is not yet fully elucidated (for the role of SET pathways in reactions of metal hydrides and alkoxides, see [22]).

Experimental Part

General. Tetraglyme (99+%, *Aldrich*) was dried prior to use through a column of alumina and stored over 4-Å molecular sieves. The 9-bromoanthracene (98%, *Aldrich*); **1** and 9,10 dibromoanthracene (98% *Aldrich* **9**) were used without further purification. All reactions were carried out in dried apparatus under N_2. GLC: *Varian-3700* GLC with a 6-foot *SE-30*-packed glass column (thermal conductivity detector) and *Hewlett-Packard-5890* GLC with a 6-foot *OV-101*-packed metal column (flame-ionization detector); peak areas were corrected by the appropriate response factors; standard deviations reported are on GLC runs in triplicate. TLC: *Merck* precoated (0.25 mm) *F-254* plates. M.p.: uncorrected. ^{1}H- and ^{13}C-NMR spectra: *Varian-XL-500* spectrometer; ^{1}H at 499.84 MHz; ^{13}C at 125.70 MHz with full ^{1}H-decoupling; δ in ppm rel. to tetramethylsilane, where a positive sign is downfield from the standard; *J* in Hz. GC-MS: *Finnigan-8200* spectrometer.

General Procedure: The molar ratios of **1**, **7**, and the base used are collected in the *Table*. To a suspension of 10 mmol of hydride base in 20 ml of tetraglyme was added dropwise (syring) a soln. of 10 mmol of **7** in 10 ml of tetraglyme. The mixture was heated at 30° until H_2 evolution was complete and then cooled, and 10 mmol of **1** were

added. The mixture was then heated to 150° with a thermostated oil bath, and samples were removed with a syringe as a function of time, quenched in 20 ml of H_2O, and acidified with dil. HCl soln. The precipitate was collected by filtration. The product composition was determined by GLC.

9-(Phenylthio)anthracene (**3**). *Method A:* A mixture of 2.20 g (20 mmol) of **7** and 2.57 g (10 mmol) of **1** in 30 ml of tetraglyme was heated at 150° for 11 h. The mixture was poured into 700 ml of ice/H_2O, acidified with dil. HCl soln. the solid collected by filtration, and the crude product purified by recrystallization from i-PrOH to give 2.20 g (77%) of crystalline **3** that was identical in every respect to the compound previously reported. M.p. 98–100° ([4]: 98–100°; [23]: 100.5–102°). ^{1}H-NMR (500 MHz, (D_6)benzene): 6.72 (*m*, 3 H); 6.94 (*m*, 2 H); 7.21 (*m*, 4 H); 7.75 (*m*, 2 H); 8.22 (*s*, 1 H); 9.89 (*m*, 2 H).

Method B: To a suspension of 2.24 g (20 mmol) of *t*-BuOK in 20 ml of tetraglyme were added dropwise 2.20 g (20 mmol) of **7** (exothermic reaction). The mixture was stirred for 15 min. To the resultant nearly homogeneous mixture were added sequentially 2.57 g (10 mmol) of **1** and 10 ml of tetraglyme. The mixture was heated at 150° for 2 h, then cooled, and poured into 500 ml of H_2O. The resultant aq. suspension was acidified with dil. HCl soln. and the solid collected by filtration and purified by recrystallization from i-PrOH to give 1.72 g (60%) of light-yellow needles, identical in every respect to that prepared by *Method A*.

9,10-Bis(phenylthio)anthracene (**10**). *Method A:* As described for **3**, **10** was prepared from 1.008 g (3 mmol) of **9**, 1.10 g (10 mmol) of **7**, and 15 ml of tetraglyme. The product was recrystallized from $CHCl_3$ to give 0.90 g (76%) of a yellow crystalline solid, identical in every respect to the compound previously reported. M.p. 212–213° ([24]: 212°). ^{1}H-NMR ($CDCl_3$): 6.97 (*d*, 4 H); 7.06 (*m*, 2 H); 7.13 (*m*, 4 H); 7.58 (complex *m*, 4 H); 8.97 (complex *m*, 4 H). ^{13}C-NMR ($CDCl_3$): 125.1, 126.4, 127.2, 127.6, 128.9, 129.7, 135.1, 138.2.

Method B: As described for **3**, **10** was prepared from 3.37 g (30 mmol) of *t*-BuOK, 3.31 g (30 mmol) of **7**, and 3.36 g (10 mmol) of **9**. The product was recrystallized from $CHCl_3$ to give 3.39 g (86%) of a yellow crystalline solid, identical in every respect to that prepared by *Method A*.

The authors wish to thank Dr. *Kenneth Ng* for the GC-MS work, and *Sylvia R. Mazzella* for assistance in running the GLC. This work was supported in part by the *Pace University Kenan Research Fund.*

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