(3 H, m, phenyl); $^{19}$F NMR (TFA ext ref) $\delta$ 4.313 (3 F, br s, $CF_3$), -108.21 (1 F, m, C*H*F); capillary GC (DB 17) retention time, 47.99 min.

**(*S*)-3-Fluorononan-1-ol, (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetate:** $^1$H NMR $\delta$ 1.97 (2 H, m, $CHFCH_2CH_2OCO$), 3.528 (3 H, q, $J_{HF}$ = 1.2 Hz, $CH_3O$), 4.45 (1 H, m, C*H*F, 2 H, m, $CHFCH_2CH_2OH$), 7.48 (2 H, m, phenyl), 7.4 (3 H, m, phenyl); $^{19}$F NMR (TFA ext ref) $\delta$ 4.258 (3 F, br s, $CF_3$), -107.8 (1 F, m, C*H*F); capillary GC (DB 17) retention time, 48.28 min.

The mass spectrum (CI, ether) for racemic Mosher esters had *m/e* 453 ($(M + 75)^+$). The mass spectrum (EI, 70 eV) had *m/e* 378 ($M^+$).

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**Supplementary Material Available:** $^1$H NMR and CI and EI mass spectra for the MPTA esters of the two enantiomeric 3-fluorononan-1-ols (4 pages). Ordering information is given on any current masthead page.

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## MeCN Is a Better Solvent Than $Me_2SO$ for Electrochemically Induced $S_{RN}1$ Substitution Reactions with Chalcogenophenoxide Anions

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Although the synthesis of aromatic substituted derivatives **1** by $S_{RN}1$ substitution (eqs 1–4)[1] is usually carried out in liquid ammonia where the hydrogen abstraction reaction (5) does not occur, dimethyl sulfoxide (DMSO) is considered as the solvent of choice among other aprotic solvents due to its low reactivity toward aryl radicals.[2]

$$ArX + e \rightleftarrows [ArX]^{\bullet -} \quad (1)$$

$$[ArX]^{\bullet -} \xrightarrow{k_1} Ar^{\bullet} + X^- \quad (2)$$

$$Ar^{\bullet} + Nu^- \xrightarrow{k_2} (ArNu)^{\bullet -} \quad (3)$$

$$(ArNu)^{\bullet -} + ArX \rightleftarrows \underset{\mathbf{1}}{ArNu} + [ArX]^{\bullet -} \quad (4)$$

$$Ar^{\bullet} + SH \xrightarrow{k_H} ArH + S^{\bullet} \quad (5)$$

$$ArX + PhE^- \xrightarrow[S_{RN}1]{} \underset{\mathbf{2}}{ArEPh} + X^- \quad (6)$$

$$Ar^{\bullet} + e \rightarrow Ar^- \quad (7)$$

Despite the fact that MeCN in slightly more reactive toward aryl radicals than DMSO,[3,4] results from Savéant, Amatore, and Thiébault[3b,5] and our group[6] have emphasized the advantages of using MeCN, which is a versatile solvent, to prepare chalcogeno derivatives **2** (E = S, Se, Te) by electrochemically induced $S_{RN}1$ substitution[7] (global reaction 6). Indeed, when the electrophilic ability of the intermediate Ar• radical is reinforced by the presence of electron-withdrawing groups such as nitrile and carbonyl functions, the key step (3) is diffusion controlled in MeCN as well as in DMSO and so the hydrogen abstraction reaction (5) becomes negligible and substitution occurs almost quantitatively as long as the cathodic reaction (7) is avoided.

Even for unactivated aryl radicals Ar• (Ar• = 4-biphenyl, 2-fluorenyl, 9-anthryl), seleno and telluro derivatives were isolated in yields ranging from 53 to 74% in MeCN.[6d] Furthermore, during the electrochemical synthesis of the 9-(phenylchalcogeno)anthracene (a, thio; b, seleno; c, telluro) derivatives **3a–c** where the nucleophilic attack (3) was not diffusion controlled, we have observed that the synthesis proceeds in better yields in MeCN than in DMSO.[6d,g] In other words, the results indicate that the ratios $k_2/k_H$ are higher in MeCN than in DMSO since the key step (3) and the reaction (5) are the only competing reactions. For instance, this ration is 5.3 ± 0.3 times higher in MeCN than in DMSO when the electrochemical synthesis of **3a,b** is carried out, as shown by cyclic voltammetry (Table I).[6g]

Surprisingly, an opposite effect was found by Savéant et al.[5b] when the electrochemical synthesis of 1-(phenylthio)naphthalene (**4**) was carried out. Indeed, **4** was isolated in almost quantitative yield in DMSO and in 32% yield in MeCN, together with 40% naphthalene (HPLC determination), when 1-BrNaph was reduced in the presence of $PhS^-$ in excess ($10^{-1}$ M; 10 equiv). During these electrolyses, the key step (3) was in competition with two side reactions (5 and 7) since the intermediate $BrNaph^{\bullet -}$ radical anion was unstable ($k_1 = 2 \times 10^8$ $s^{-1}$ in DMSO), and so Naph• was generated close to the electrode where it was reduced and then protonated to naphthalene. With the assumption that the unknown cleavage rate, $k_1$, of the 1-$BrNaph^{\bullet -}$ radical anion in MeCN was the same as in DMSO, it was concluded that $k_2/k_H = 15$ $M^{-1}$ in MeCN and 40 $M^{-1}$ in DMSO. The same latter value was also found by Helgée and Parker in DMSO.[4]

In order to be able to determine the ratio $k_2/k_H$ in MeCN with no assumption concerning $k_1$ in this solvent, we have carried out the indirect reduction of 1-bromonaphthalene in MeCN and DMSO in the presence of a redox mediator (med) in order to avoid the cathodic side reaction (7). Indeed, under such conditions, $[ArX]^{\bullet -}$ and therefore Ar• are generated in the bulk of the cathodic solution through the following reactions: med + e ⇄ $med^{\bullet -}$ and $med^{\bullet -}$ + ArX ⇄ med + $[ArX]^{\bullet -}$.[1c,7-9] Hence, the

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Table I. Kinetic Data for Reactions of 9-Anthr• and 1-Naph• Radicals in MeCN and DMSO

| | | reactant/MeCN | | | reactant/DMSO | | | MeCN/DMSO |
|---|---|---|---|---|---|---|---|---|
| Ar• | reactant | $10^{-7}k_H$ ($s^{-1}$) | $k_2/k_H$ ($M^{-1}$) | $10^{-9}k_2$ ($M^{-1}$ $s^{-1}$) | $10^{-7}k_H$ ($s^{-1}$) | $k_2/k_H$ ($M^{-1}$) | $10^{-9}k_2$ ($M^{-1}$ $s^{-1}$) | $k_2/k_2$ |
| 9-Anthr• | MeCN | 2[a] | | | | | | |
| | DMSO | | | | 0.85[a] | | | |
| | $PhS^-$ | | 330[b] | 6.6[b] | | 56[a] | 0.45[a] | 14 |
| | $PhSe^-$ | | 406[b] | 8.1[b] | | 77[b] | 0.65[b] | 12 |
| | $PhTe^-$ | | | | | 180[b] | 1.5[b] | |
| 1-Naph• | MeCN | 23[a] | | | | | | |
| | | 0.48[c] | | | | | | |
| | DMSO | | | | 10[a] | | | |
| | | | | | 0.42[c] | | | |
| | $PhS^-$ | | 440 | 100[d] | | 38 | 3.8[f] | 26[a] |
| | | | (15[e]) | | | (40[c,e]) | | |
| | | | | 2.1[g] | | | 0.16[h] | 13[c] |

[a] From ref 3a. [b] From ref 6g. [c] From ref 4. [d] When $k_H = 2.3 \times 10^8$ $s^{-1}$ (cf. ref 3a). [e] From ref 3b. [f] When $k_H = 1.0 \times 10^8$ $s^{-1}$ (cf. ref 3a). [g] When $k_H = 4.8 \times 10^6$ $s^{-1}$ (cf. ref 4). [h] When $k_H = 4.2 \times 10^6$ $s^{-1}$ (cf. ref 4).

naphthyl radicals were generated in the bulk of the cathodic solution and the yields of the substituted naphthalene 4 reflected the true $k_2/k_H$ values. The results depicted in the following text lead to results similar to those obtained by our group in MeCN and DMSO for the couple 9-Anthryl•/$PhE^-$, and so they confirm the inauspicious influence of DMSO upon the electrochemically induced $S_{RN}1$ substitution involving Ar•/$PhE^-$ couples.

## Results and Discussion

The choice of benzophenone as redox mediator for the indirect reduction of 1-bromonaphthalene resulted from a preliminary voltammetric study at a glassy carbon stationary disc electrode (SDE). In MeCN and DMSO, the cathodic peak current of benzophenone increased upon addition of 1-BrNaph, whereas the corresponding anodic peak current decreased. In both solvents, large-scale electrolyses of 1-BrNaph proceeded in four steps. First, a preelectrolysis of the solvent containing $Bu_4NPF_6$ (0.1 M) as supporting electrolyte was performed in order to suppress any traces of electroactive impurities. Second, PhSSPh (2 mmol) was added and reduced to $PhS^-$. Third, benzophenone (1 mmol) and 1-BrNaph (4 mmol) were added, and a working potential of −1.7 (MeCN) or −1.65 V (DMSO) was applied. At these potentials, benzophenone was the only reducible species. Fourth, the benzophenone radical anions and the $PhS^-$ anions in excess were oxidized anodically to benzophenone and PhSSPh, respectively, by shifting the applied potential from −1.7 (MeCN) or −1.65 V (DMSO) to 0 V. After dilution with water of the cathodic solution and a very careful extraction of the electrolysis products by diethyl ether, a sample of the crude product was analyzed by GC. When the electrolysis was carried out in MeCN, the crude product corresponded to a mixture of naphthalene (0.146 mmol), 1-BrNaph (1.243 mmol), 4 (2.396 mmol), PhSSPh (0.534 mmol), benzophenone (0.211 mmol), and β-phenylcinnamonitrile (0.49 mmol). It is well-established that this latter compound was generated catalytically in MeCN by reduction of benzophenone in the presence of traces of impurities such as water or bases.[10] Since 3.785 mmol of naphthalene and substituted naphthalene derivatives were analyzed by GC, that is to say 95% of the total expected amount, it was reasonably assumed that traces of naphthalene (≤5%) were lost by sublimation under vacuum. On the other hand, taking into account that some 1-BrNaph was recovered, it was concluded that 4 was prepared in 87% yield (GC determination). When the electrolysis was repeated in DMSO, the yield of 4 dropped to 49% since the crude product contained a mixture of naphthalene (1.415 mmol), 1-BrNaph (0.181 mmol), and 4 (1.888 mmol). In this electrolysis, only 3.484 mmol (87%) of naphthalene and its derivatives were analyzed by GC, suggesting again that a small amount of naphthalene (≤13%) was lost by sublimation under vacuum.

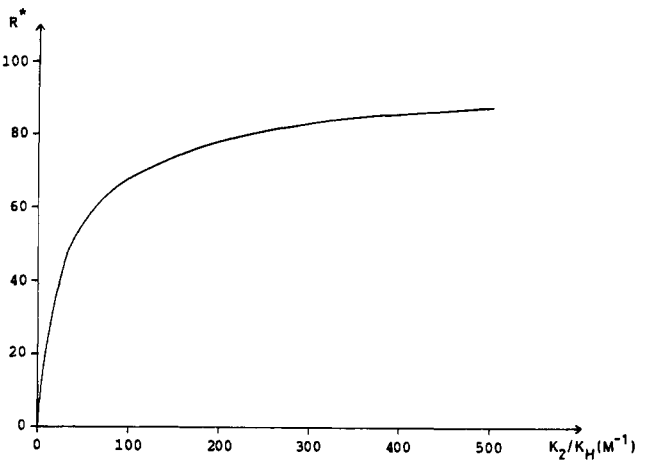


Figure 1. Variation of $R^*$ of 2 with the ratio $k_2/k_H$ from eqs 9 and 10 when $C_i$ of ArX and $PhE^-$ is $4 \times 10^{-2}$ M.

When the nucleophile is in excess and its concentration ($Nu^-$) maintained constant during electrolysis, it is possible to determine the ratio $k_H/k_2$ from the yield $R$ (%) of the substitution compound by applying eq 8.[3b] Under our experimental conditions, this equation could not be applied since only 1 equiv of $PhS^-$ ($4 \times 10^{-2}$ M) was present at the beginning of the electrolysis. We have shown recently[6g] that a good approximate value of $k_H/k_2$ can be obtained from eqs 9 and 10 where $C_i$ is the initial concentration of ArX and $Nu^-$ (1 equiv) and $R^*$ (%) the yield of ArNu.

$$R = \frac{100}{1 + k_H/(k_2 Nu^-)} \tag{8}$$

$$R^* = 100\left(1 + \frac{k_H/k_2}{C_i - C_f} \ln \frac{k_H/k_2 + C_f}{k_H/k_2 + C_i}\right) \tag{9}$$

$$C_f = \frac{C_i k_H/k_2}{C_i + k_H/k_2} \tag{10}$$

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When $C_i = 4 \times 10^{-2}$ M, the dependence of $k_2/k_H$ on R* is shown in Figure 1.

Since the thioether 4 was isolated in 49% yield in DMSO and 87% yield in MeCN, we could derive from Figure 1 that $k_2/k_H = 38$ $M^{-1}$ in DMSO and 440 $M^{-1}$ in MeCN. The former value is almost identical with the value determined by Parker et al.[4] and Savéant et al.[3b] in DMSO ($k_2/k_H$ = 40 $M^{-1}$) (Table I) whereas the latter differs by a factor of 29 from the value proposed by Savéant et al. ($k_2/k_H$ = 15 $M^{-1}$), assuming that $k_1$ was the same in DMSO and MeCN. Our results suggest that the cleavage rate of 1-BrNaph$^{\bullet-}$ would be higher in MeCN than in DMSO, as in the case of 1-INaph$^{\bullet-}$ radical anion,[3a] and so the moderate yield of 4 (32%) obtained in MeCN in the absence of mediator would result from the side reaction (7). In Table I, we have also indicated the absolute $k_2$ values derived from the $k_H$ values proposed by Saveant et al.[3a] and Parker et al.[4] In MeCN, the $k_2$ value derived from Saveant's data exceeds the limiting diffusion-controlled value ($k_d = 2 \times 10^{10}$ $M^{-1}$ $s^{-1}$), suggesting that the rate of hydrogen abstraction is at least five times slower ($k_H \leq 4.6 \times 10^7$ $s^{-1}$) than the proposed value. The same remark probably holds in DMSO. Finally, a comparison of the $k_2$ values in MeCN and DMSO show that the nucleophilic attack of PhS$^-$ toward the 1-Naph$^\bullet$ radical is 26 or 13 times faster in MeCN than in DMSO, depending on the data provided by Saveant et al.[3a] or Parker et al.[4] (Table I).

These latter results are consistent with those previously obtained for the 9-Antr$^\bullet$/PhE$^-$ couples and confirm the unfavorable influence of DMSO as far as the PhE$^-$ nucleophiles are involved. This influence cannot be explained from thermodynamic considerations such as the donor number values (DN) of the solvents (DN = 29.8 for DMSO and 14.1 for MeCN).[11] Indeed, such data suggest that decomposition of the unstable ArX$^{\bullet-}$ radical anion is more rapid in DMSO than in MeCN,[3a] due to a stronger solvatation in DMSO of the generated Ar$^\bullet$ radical, which thus becomes less electrophilic and therefore less inclined to nucleophilic attacks. Thus, $k_1$ should increase and $k_2$ decrease in DMSO, which is not compatible with the experimental results observed in the case of 1-BrNaph. Therefore, a kinetic effect of the solvent upon the activation barrier has to be considered. A stabilization of the transition state or a decrease of the solvent reorganization energy can be involved if the ArX$^{\bullet-}$ cleavage and the ArNu$^{\bullet-}$ formation are considered as intramolecular dissociative and associative electron transfers.[12-15]

## Experimental Section

Analytical-grade MeCN and DMSO were purchased from SDS. Acetonitrile was carefully dried on neutral alumina. The starting materials were of commercial origin. Pure thioether 4 was obtained by column chromatography (Kieselgel with $CH_2Cl_2$/hexane = 5/95 as eluant) of the crude product isolated after electrolysis of 1-bromonaphthalene in MeCN (yield 68%). β-Phenylcinnamonitrile was prepared by cathodic reduction of benzophenone in MeCN.[10]

An Amel 552 potentiostat (output voltage 200 V at full load) and a Tacussel IG5-N integrator were used in coulometry and preparative electrolysis. All the potentials referred to the aqueous saturated calomel electrode (SCE). The electrochemical synthesis of 4 was carried out in a H-type cell, the three compartments of which were separated by ion-exchange membranes Ionax MA 3475 (anodic side) and MC 3470 (cathodic side). The cathode was a graphite cloth of cylindrical shape and the anode a Pt grid. The cathodic solution (100 mL) was stirred mechanically and deaerated with argon prior to and during electrolysis. Helium was the gas vector of a Shimatzu GC 14A chromatograph equipped with a CR 6A detector (25 m × 0.25 mm capillary column DB1). The temperature of the injector and detector (FID) was 300 °C. The temperature of the column was changed from 80 to 250 °C (5 °C per min) then maintained at 250 °C.

**Electrochemical Synthesis of 4 in MeCN.** After a preelectrolysis of the solvent containing $Bu_4NPF_6$ (0.1 M) in order to suppress any electroactive impurities, PhSSPh (2 mmol; $2 \times 10^{-2}$ M) was introduced and reduced to PhS$^-$. The potential had to be changed from −1.0 to −2.05 V, whereas the faradaic current dropped from 90 mA (initial value) to a negligible value, after consumption of 390 C (4 mmol of electrons). The electrolysis was interrupted, and 1-bromonaphthalene (4 mmol) together with benzophenone (1 mmol) were added and reduced at −1.7 V. The faradaic current dropped from 24 mA (initial value) to 13 mA after consumption of 155 C (1.60 mmol of electrons). Finally the potential was changed from −1.7 to 0 V in order to oxidize the benzophenone radical anions and the PhS$^-$ anions in excess. The electrolysis was stopped after consumption of 213 C (2.81 mmol of electrons). The cathodic solution was diluted with water, and the electrolysis products were extracted with diethyl ether. After the solution was dried and the ether removed, the crude product was purified on a Soxhlet with diethyl ether in order to suppress any traces of supporting electrolyte. The ethereal solution was dried, ether was removed, and the crude product was dried under vacuum at room temperature for 1 day. A sample of the crude product (1.147 g) was analyzed by GC with phthalonitrile as internal standard and compared to a reference mixture containing β-phenylcinnamonitrile in addition to the expected compounds. Thus, the crude product was a mixture of naphthalene (17.3 mg; 0.146 mmol), 1-BrNaph (257.4 mg; 1.243 mmol), 4 (566.4 mg; 2.396 mmol), PhSSPh (116.5 mg; 0.534 mmol), benzophenone (38.5 mg; 0.211 mmol), and β-phenylcinnamonitrile (100.0 mg; 0.49 mmol).

**Electrochemical Synthesis of 4 in DMSO.** The preceding experiment was repeated in DMSO. After a preelectrolysis then generation of PhS$^-$ (4 mmol), the indirect reduction of 1-BrNaph (4 mmol) by benzophenone (1 mmol) was carried out at −1.65 V. The faradaic current dropped from 26 mA (initial value) to 5 mA after consumption of 270 C (2.87 mmol of electrons). The anodic step consumed 168 C (1.75 mmol of electrons). From a sample of the crude product (0.822 g) which was isolated as previously, a GC determination indicated that the crude product was a mixture of naphthalene (167 mg; 1.415 mmol), 1-BrNaph (37.5 mg; 0.181 mmol), PhSSPh (94.2 mg; 0.431 mmol), 4 (446.1 mg; 1.888 mmol), and benzophenone (88.5 mg; 0.485 mmol).

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# Correlation of the Rates of Solvolysis of the Benzyldiphenylsulfonium Ion[1]

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As an aid to assessing the extent of nucleophilic participation by the solvent at the transition state for solvolytic displacement reactions, several scales of solvent nucleophilicity[2] for use within the extended Grunwald-

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