

Electrochemical Reduction of Activated Olefins in Deuteriated Solvents. II. A Regioselective Deuteriation Catalytic Process from α,β -Ethylenic Aryl Sulfones

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Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

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The title compounds were electrochemically reduced in aprotic dimethyl sulfoxide- d_6 , acetonitrile- d_3 or organic solvents containing heavy water. When a catalytic amount of charge passed through the cell, α -deuteriation of olefins occurred in high yield. Since both chemical and electrochemically formed bases were found to be totally inefficient in the performance of such deuteriation, a radical chain process is tentatively proposed. During attempted total reduction of substrates, tetradeuteriated dimers were isolated, from which information on the reduction mode and coupling process can be obtained.

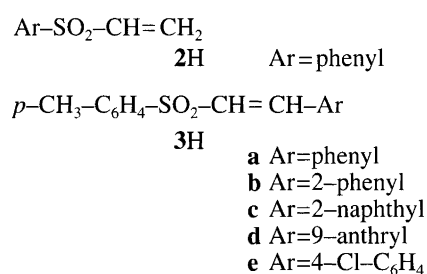
The electrochemical reactivity of sulfones and sulfoxides is now a rather well documented field.¹ More specifically, cathodic coupling and electrocatalytic electrodimmerization of α,β -ethylenic sulfones in aprotic solvents have been achieved.^{2,3} With regard to the cathodic behaviour of α,β -ethylenic sulfoxides **1**, it has recently been shown⁴ that 'activation by means of electron transfer' in deuteriated solvents (DS) such as dimethyl sulfoxide- d_6 (DMSO) and acetonitrile- d_3 (AN) leads quantitatively to α -monodeuteriated compounds according to the following eqn. (1).

The aim of the present paper is to study similarly the cathodic behaviour of α,β -ethylenic sulfones **2** and **3** both in deuteriated solvents and in DMSO with heavy water added, in order to check whether deuteriation, already found with sulfoxides **1**, was also relevant to the behaviour of unsaturated sulfones.

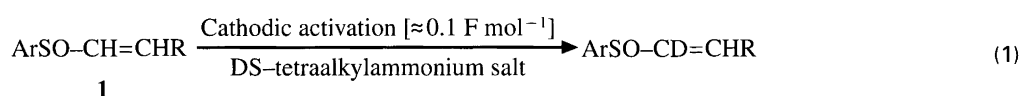
Experimental

Sulfones synthesis. The synthesis of sulfones **2H** and **3H** is fully described in the literature: sulfone **2H** was pre-

pared according to Ref. 5, sulfone **3aH** according to Ref. 6 and substrate **3b-eH** according to Ref. 7. ¹H NMR spectra were recorded on a JEOL GSX 270 WB (270 MHz) in CDCl₃ or CD₂Cl₂ with Me₄Si as an internal reference. Mass spectra were obtained with a Varian MAT 311 spectrometer.



Electrolytes. DMF and DMSO were distilled and kept over molecular sieves 3 Å. DMSO- d_6 (99.8%), AN- d_3 (99.8%) and D₂O (100%) were purchased from 'Solvents-



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Documentation–Syntheses' (SDS). Salts such as Et_4NClO_4 (TEAP) and Bu_4NBF_4 (TBATFB) were easily prepared; they were recrystallized from water and then dried under vacuum. LiClO_4 (95%) was bought from Aldrich and used without further purification.

Voltammetry. Current–voltage curves were obtained by use of a PAR model 362 potentiostat equipped with a X–Y Kipp–Zonen recorder. The three electrode Metrohm cell was furnished with a hanging mercury drop as working electrode (cathode), a counter electrode made of platinum (Pt wire or gauze) and a reference system: $\text{Ag}/\text{AgI}/\text{I}^-$ 0.1 M in DMF. This reference was the only one used throughout the described work.

Coulometry and macroelectrolysis. Potentiostatic electrolyses were achieved in a two-compartment Metrohm cell (separator: glass frit of porosity 5). The working electrode was a mercury pool (area: ca. 10 cm^2), the counter electrode being a platinum gauze. The electrolysis cell was connected to a Tacussel PRT 40–1X potentiostat equipped with a Tacussel IG5–LN integrator.

Work-up and purification. At the end of the electrolyses conducted in deuteriated solvents ($\text{DMSO}-d_6$ and $\text{AN}-d_3$) the products were not isolated; results given in Table 2 correspond to ^1H NMR analysis achieved directly from electrolytic solution. In contrast, when heavy water was used as the deuterium donor (by addition to DMSO), the typical procedure was as follows: 1 g of **3H** was dissolved in 40 ml of DMSO containing 0.1 M LiClO_4 and 2 ml D_2O . The working electrode was, in all cases, a stirred mercury pool (area: 10 cm^2). Applied working potentials are all listed in Table 3. Experimentally, electrolyses were stopped when 0.1 F mol^{-1} of sulfone had passed. Afterwards, the catholyte solution was extracted with methylene chloride and then washed with water. Dried extracts were chromatographed on silica gel (Merck 60 H) using cyclohexane–ethyl acetate as the eluent for products **3D**, and methylene chloride–ethyl acetate mixture for dimers **4D** according to the product solubility.

Results of electrolyses. (A) *Electrochemical activation.* **2H** reduced at 0.1 F mol^{-1} in CD_3CN or $\text{DMSO}-d_6$ to give (1-deuterioethenyl)phenyl sulfone **2-d₁**, lit.⁸

3aH gave (E)-4-methylphenyl 1-deuterio-2-phenylethenyl sulfone **3aD**, m.p. (isopropyl ether) 120°C . ^1H NMR: δ 2.40 (s, 3 H), 7.20 (d, 2 H, $^3J=8.2\text{ Hz}$), 7.26 (m, 3 H), 7.33 (dd, 2 H, $^3J=7.5\text{ Hz}$), 7.62 (t, 1 H, $^3J_{\text{HD}}=2\text{ Hz}$), 7.82 (d, 2 H, $^3J=8.2\text{ Hz}$).

3bH gave (E)-4-methylphenyl 1-deuterio-2-(2-pyridyl)ethenyl sulfone **3bD**, m.p. (isopropyl ether) 100°C . ^1H NMR: δ 2.40 (s, 3 H), 7.20 (d, 2 H, $^3J=8.2\text{ Hz}$), 7.30–7.50 (m, 3 H), 7.70 (t, 1 H, $^3J_{\text{HD}}=2\text{ Hz}$), 7.90 (d, 2 H, $^3J=8.2\text{ Hz}$), 8.60 (dd, 1 H, H_α pyridyl).

3cH gave (E)-4-methylphenyl 1-deuterio-2-(2-naphthyl)ethenyl sulfone **3cD**, m.p. (ethanol) 160°C . ^1H NMR: δ 2.40 (s, 3 H), 7.35 (d, 2 H, $^3J=8.2\text{ Hz}$),

7.55–7.65 (m, 7 H, naphthyl), 7.80 (t, 1 H, $^3J_{\text{HD}}=2\text{ Hz}$), 7.9 (d, 2 H, $^3J=8.2\text{ Hz}$).

3dH gave (E)-4-methylphenyl 1-deuterio-2-(2-anthryl)ethenyl sulfone **3dD**, m.p. (ethanol) 171°C . ^1H NMR: δ 2.40 (s, 3 H), 7.30–7.60 (m, 7 H), 7.90–8.10 (m, 5 H), 8.40 (s, 1 H, H^{10} anthryl), 8.60 (t, 1 H, $^3J_{\text{HD}}=2\text{ Hz}$).

3eH gave (E)-4-methylphenyl 1-deuterio-2-(4-chlorophenyl)ethenyl sulfone **3eD**, m.p. (ethanol) 150°C . ^1H NMR: δ 2.40 (s, 3 H), 6.67 (t, 1 H, $^3J_{\text{HD}}=2\text{ Hz}$), 7.30 (d, 2 H, $^3J=8.2\text{ Hz}$), 7.50 (s, 4 H, chlorophenyl), 7.9 (d, 2 H, $^3J=8.2\text{ Hz}$).

(B) *Exhaustive reduction of 3aH.* Hydrodimer (\pm)-**4aD**, m.p. (ethanol) 172°C . ^1H NMR: δ 2.40 (s, 6 H), 3.78 (s, 2 H, $\text{C}_D\text{2CH}$), 6.65 (dd, 4 H, $^3J=7.5\text{ Hz}$), 7.03–7.16 (m, 6 H), 7.22 (d, 4 H, $^3J=8.2\text{ Hz}$), 7.58 (d, 4 H, $^3J=8.2\text{ Hz}$). MS: m/z 416 ($M-\text{C}_6\text{H}_5-\text{CH}-\text{CD}_2$), 261 ($M/2$).

Hydrodimer *meso*-**4aD**, m.p. (CHCl_3) 297°C . ^1H NMR (CD_2Cl_2) δ : 2.35 (s, 6 H), 3.15 (s, 2 H), 6.95 (dd, 4 H, $^3J=7.5\text{ Hz}$), 7.12 (d, 4 H, $^3J=8.2\text{ Hz}$), 7.27 (m, 10 H). MS: m/z 367 ($M-\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{SO}_2$), 261 ($M/2$).

Results

Sulfones **2H** and **3H** are readily reducible at a mercury cathode, especially when conventional aprotic solvents containing tetraalkylammonium salts are used. Substrates **3H** generally exhibit at least three steps (see Table 1). The two first steps are monoelectronic (consecutive formation of the anion radical – reversible step at a sweep rate $v \geq 0.5\text{ V s}^{-1}$ – and of the dianion – irreversible peak as depicted in Fig. 1). When a proton donor like phenol was added in excess to the solution, two main reduction steps were observed, the first one accounting for the two-electron cleavage of the C–S bond, and the second for the bielectronic saturation of the transient olefin.

The electrochemical behaviour of sulfone **2H** has already been discussed elsewhere² and was found to correspond to a very fast [2+2] cyclodimerization catalyzed at the level of the anion radical by electron transfer. Therefore, the electrochemical step (low sweep rates) does not account for the ethylenic sulfone but for its cyclodimer.

There was no change in the voltammetric behaviour of sulfones **2H** and **3H** when deuteriated solvents were used instead of more conventional aprotic solvent/electrolyte couples. However, some discrepancies were observed when macroelectrolyses were stopped when a very limited amount of electricity (i.e., 0.1 mol of electrons per mole of sulfone) had passed through the cell. Thus with sulfone **2H**, electrolysis results in $\text{DMSO}-d_6$ and $\text{AN}-d_3$ are gathered in Table 2. In deuteriated acetonitrile containing tetraalkylammonium salt, deuteriation of **2H** occurred but in moderate yields. In contrast when $\text{DMSO}-d_6$ containing lithium perchlorate was used, deuteriation was not observed but previously reported

Table 1. Voltammetry of some unsaturated sulfones **3H** and **3D** (concentration: 2×10^{-3} M) in aprotic (DMF containing 0.1 M Bu_4NBF_4) and protic (addition of phenol) media. Mercury microelectrodes. Sweep rate: 100 mV s^{-1} . Reference: $\text{Ag}/\text{AgI}/\text{I}^-$ 0.1 M-DMF. *N.B.*: in the presence of 5% water or 5% D_2O , no significant change in peak potentials toward values found for aprotic solvent was found.

Substrates	Aprotic solvent				Protic solvent (4×10^{-3} M + phenol)	
	E_1/V	E_2/V	E_3/V	E°/V	E_1/V	E_2/V
3aH (Z)	-1.29 (1e)	-1.87 (1e)	-2.06	-1.26	-1.17 (2e)	-2.03 (2e)
3aH (E)	-1.31 (1e)	-1.91 (1e)	-2.10	-1.28	-1.22 (2e)	-2.02 (2e)
3bH	-1.10 (1e)	-1.85 (1e)	-2.01	-1.07		
3aD (E)	-1.25 (1e)	-1.82 (1e)	2.04	-1.22	-1.19 (2e)	-2.02 (2e)
3bD	-1.08 (1e)	-1.57 (1e)	-1.81	-1.05	-1.05 (2e)	-1.76 (2e)
3cD	-1.16 (1e)	-1.55 (1e)	-1.82	-1.13	-1.12 (2e)	-1.72 (2e)

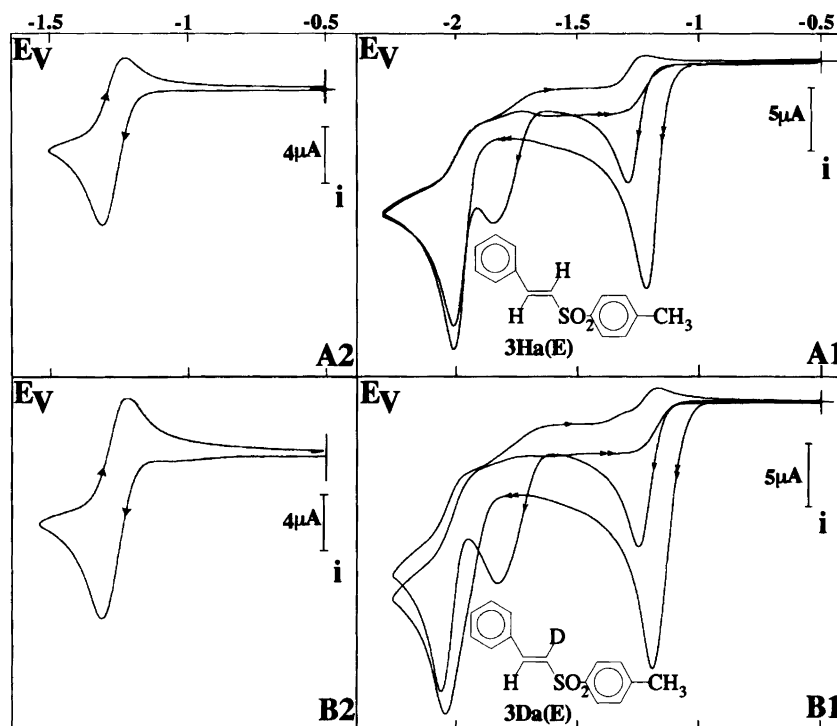


Fig. 1. Cyclic voltammetry of **3aH** (E) and **3aD** (E) at a stationary mercury microelectrode. Reference electrode: $\text{Ag}/\text{AgI}/\text{I}^-$ 0.1 M. Electrolyte: DMF-0.1 M Bu_4NBF_4 ; (A1) and (A2) for compound **3aH** (E) (2×10^{-3} M); (B1) and (B2) for compound **3aD** (E) (2×10^{-3} M). (A1) and (B1) sweep rate: 0.1 V s^{-1} . (A2) and (B2) sweep rate: 0.5 V s^{-1} . \blacktriangleright , in aprotic solution. $\blacktriangleright\blacktriangleright$, in a solution containing 4×10^{-3} M phenol.

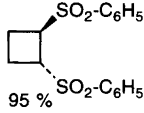
cyclodimerization was found to occur in quantitative yield.

With sulfones **3H**, the deuteration reaction could not be specifically achieved in only deuterated solvents. When stopped after a small amount of electricity had been consumed, macroelectrolysis of **3H** with (Z+E) mixtures in DMSO or DMF, showed the total disappearance of the Z isomer due to the cathodic conversion of Z into E as already described for a number of olefins.^{3,9-11} Deuteration was found to occur in high yield (Table 3) only when macroelectrolytic activation of sulfones **3H** (on either the starting isomer) was accom-

plished in DMSO containing an amount (5%) of heavy water (D_2O) in addition to the supporting electrolyte. The regioselectivity of the deuteration reaction appeared to be very good. Moreover, the E isomer was always the only isolated isomer after cathodic treatment of all tested sulfones **3H**. In addition, results with sulfone **3D** (Table 1, Figs. 1 and 2) showed very similar behaviour with the parent protonated sulfones **3H**. It is worth noting, however, that a clear potential shift towards less negative values was found for the first reduction step.

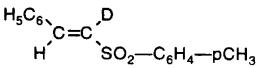
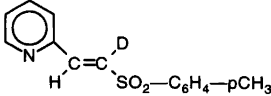
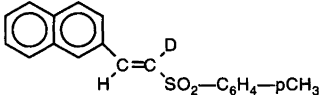
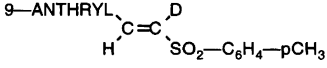
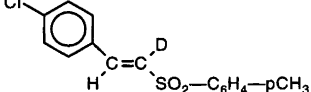
When **3aH** was reduced (potentiostatic exhaustive reduction in this case) in DMSO with 5% D_2O added,

Table 2. Cathodic activation with sulfone **2H** in deuteriated solvents.

Entry	Substrate concentration	Solvent (Electrolyte)	Working potential ^a /V	Electrical consumption /F mol ⁻¹	Products
1	5 × 10 ⁻² M	CD ₃ CN (Bu ₄ NBF ₄ 0.1 M)	-1.4	0.1	C ₆ H ₅ -SO ₂ -CD=CH ₂ 45% C ₆ H ₅ -SO ₂ -CH=CH ₂ 55%
2	5 × 10 ⁻² M	CD ₃ SOCD ₃ (LiClO ₄ 0.1 M)	-1.4	0.1	 95 %

^aReference electrode Ag/AgI/I⁻ 0.1 M-DMF.

Table 3. Electrolyses of α,β-ethylenic sulfones **3H** in DMSO-0.1 M LiClO₄ with 5% D₂O added. The electrolyses were stopped after 0.1 F mol⁻¹ of electricity had passed; two-compartment cell; mercury pool cathode (area: 10 cm²).

Starting sulfone (isomer)	Working potential ^a /V	Product deuteriated sulfones 3D	Isolated yield (%) (isomer)
3aH (<i>E</i> + <i>Z</i> or <i>E</i>)	-1.15	3aD 	95 (<i>E</i>)
3bH (<i>E</i>)	-0.95	3bD 	97 (<i>E</i>)
3cH (<i>E</i>)	-1.00	3cD 	97 (<i>E</i>)
3dH (<i>E</i>)	-0.90	3dD 	85 (<i>E</i>)
3eH (<i>E</i>)	-1.05	3eD 	95 (<i>E</i>)

^aReference electrode: Ag-AgI/I⁻ 0.1 M in DMF.

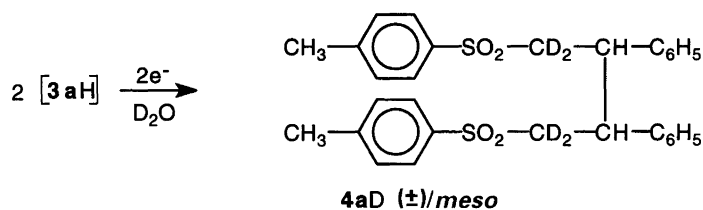
the total consumption of electricity was 1.1 F mol⁻¹. Two compounds **4aD** were isolated (crystallization from chloroform and ethanol). They were identified as the (±)-dimer (75% of isolated yield) and *meso* dimer (5%). The stereochemistry of each isomer was established by comparison with fully protonated analogues (±) *meso* and (±)-**4aH** as described in a previous paper.³

Finally, it was checked that the reduction of **3aD** in DMSO+5% D₂O (coulometric measurement:

1.05 F mol⁻¹) produced dimers **4aD** [(±)-*meso* in mixture ratio: 90:10].

Discussion

The cathodic activation and exhaustive reduction of compounds **2H** and **3H** have already been fully investigated.¹² Series **2H** was found (probably for structural reasons) to undergo catalytically unexpected cathodic



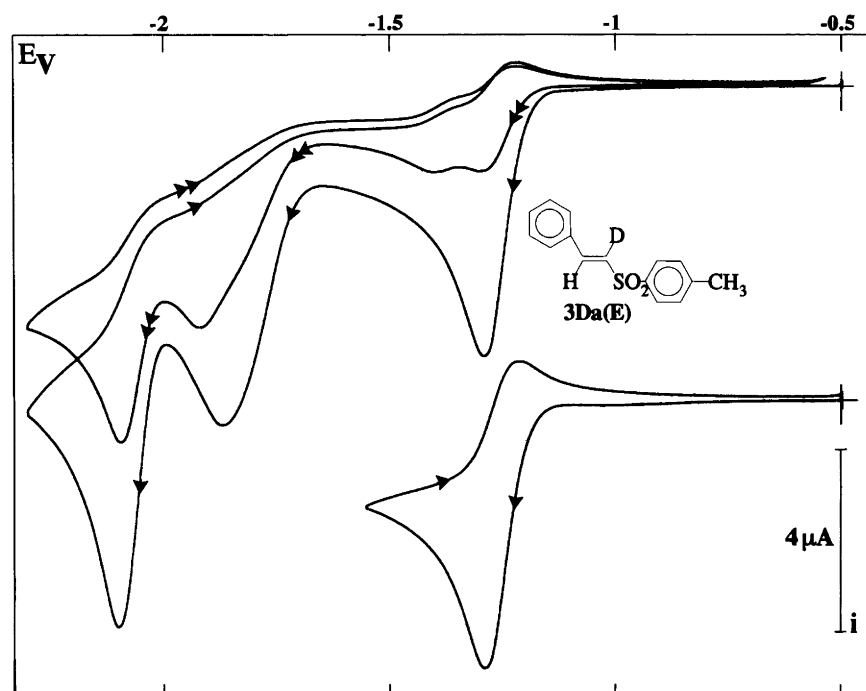
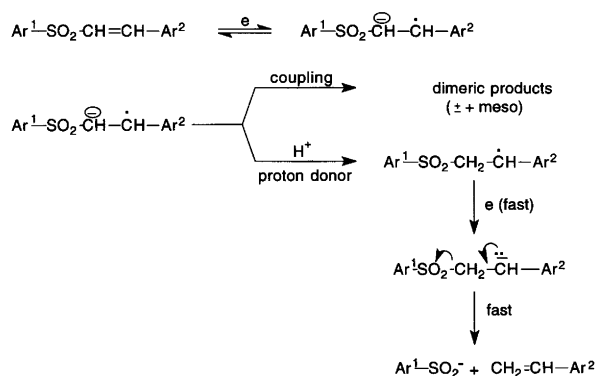


Fig. 2. Cyclic voltammetry for compound **3aD** (*E*) (2×10^{-3} M) at a stationary mercury microelectrode. Reference electrode: Ag/AgI/ I^- 0.1 M. Electrolyte: DMF-0.1 M Bu_4NBF_4 . Sweep rate: 0.1 V s^{-1} . \blacktriangleright , first sweep; $\blacktriangleright\blacktriangleright$, second sweep.

cyclodimerization, often in very high yield and under very simple experimental conditions. In contrast, compounds **3H**, when principally reduced in DMSO- $LiClO_4$, produced only acyclic dimeric forms [with a very large proportion of (\pm)-isomer]. Such a coupling reaction seemed surprising because previous work with α,β -ethylenic sulfones under similar experimental conditions resulted mostly¹³ in the cleavage of the C-S bond, by means of a β -elimination (*E*-protonation-*E*-elimination process).



Scheme 1.

The present work also demonstrates that deuteration reactions achieved electrochemically with α,β -ethylenic sulfoxides, could also be applied to the parent sulfones by using specific experimental conditions.

The most suitable conditions for a substitution of this kind were shown to be DMSO+0.1 M $LiClO_4$ with 5% D_2O added. However, the use of tetrabutylammonium

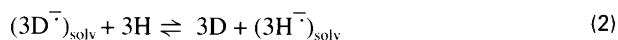
tetrafluoroborate also led to deuteration. Whatever the stereochemistry of the starting material, regioselective deuteration could occur in very good yield, leading exclusively to *E* isomer. Note that the synthesis of such deuterated sulfones (i.e., phenyl 1-deuterio-2-phenylethyl sulfone) has been mentioned in the literature¹⁴ from a more complicated reaction pathway.

What kind of mechanism could explain this deuteration process? It should be recalled first that methyl aryl sulfones are very weakly acidic.¹⁵ It is then expected that vinylic and styryl sulfones can react specifically with very strong bases. With sulfones such as **3H** in particular, a base-catalysis process could be assumed. In fact, the formation¹⁶ at low temperature of lithium salts **3Li**, which are able to react regioselectively with many kinds of electrophiles (like D_2O), has been described. More particularly at the cathode interface, very small amounts of electrogenerated bases produced during the activation phase (low electricity consumption) might trigger hydrogen-deuterium exchange catalysis in compounds **3H**. In order to check the possible effect of all kinds of bases, two series of experiments were run.

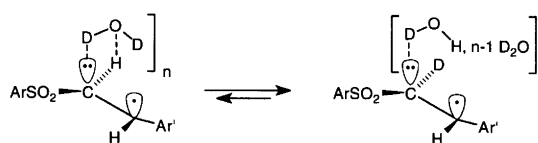
(i) *With chemical bases (without current)*. A typical procedure to test the possible action of these bases is as follows: 26 mg of **3aH** in 3 ml of DMSO-0.5 M $LiClO_4$ +0.1 ml D_2O were reacted with strong bases such as tetrabutylammonium hydroxide (0.2 equiv.) or potassium *tert*-butoxide (0.2 equiv.). After 24 h at room temperature, absolutely no reaction with **3aH** was noted (and especially no visible H-D exchange in the NMR spectrum).

(ii) *With strong electrogenerated bases.* The chosen pro-base was azobenzene (AZ). In dry DMSO, the first voltammetric step of azobenzene (formation of the anion radical) was not disturbed by addition of **3aH** (*E*) in large excess (tenfold), meaning that base $AZ^{\cdot-}$ is not strong enough to rapidly deprotonate styryl sulfones. Furthermore, no changes were observed when heavy water was added (first 2% and then 5%). In order to check the voltammetric data, macroelectrolyses were carefully carried out with **3aH** (*E*) and **3eH** as substrates according to the following procedure. Azobenzene (0.012 g, 0.06 mmol) was reduced in 4 ml DMSO + 0.1 M $LiClO_4$ + 0.2 ml D_2O in the presence of 0.1 g (about 0.4 mmol) of sulfone. The working potential of the mercury pool cathode (2 cm²) was fixed at -0.8 V (the level of the first step of AZ). After passage $0.1 F mol^{-1}$, electrolysis was stopped. After extraction according to the usual work-up, ¹H NMR analysis of both reaction products showed that neither sulfones suffered any chemical transformation.

Thus, it seems reasonable to assume that the key reaction, whatever the electrolyte cation present (Li^+ or N^+Bu_4), is the neutralization of **3H** anion radical by D_2O . In the presence of a large excess of heavy water, $3H^{\cdot-}$ would be hydrated similarly to most other anion radicals of compounds (such as aromatic compounds and activated olefins) with a suitable LUMO (see work by Savéant's group¹⁷ in this field). Deuteron-proton exchange might then occur at this level, based on the relative acid-base strength of $3H^{\cdot-}$ and $3D^{\cdot-}$ inside the heavy water shell as shown in Scheme 2, and followed by eqn. (2).



Since voltammetric curves of compounds **3H** did not present any significant discrepancies in the absence and the presence of heavy water, it seems reasonable that the propagation reaction is, in this case, rather slow and displaced toward the right-hand side by a change of solvation energy. Intrinsically, propagation should not occur since $E_{3H}^{\circ} < E_{3D}^{\circ}$. It is recalled here (in contrast with sulfoxides) that the conditions under which sulfones undergo deuteration are with added D_2O , deuteriated solvents being unable to bring about the exchange by themselves. Deuteriated *E*-isomers were obtained in all cases whatever the structure of the starting compound. However, the fast transformation *Z* → *E* via electron transfer (even in the absence of D_2O) has already been noted, and here the stereochemistry of deuteriated struc-



Scheme 2.

tures cannot give further information about the global mechanism.

On the other hand, it was also interesting to follow the cathodic stability of compounds **3D** in regular electrolytes containing DMF or DMSO. For sweeps (or multi-sweeps) achieved at the level of the anion radical, no changes in this step were evident by cyclic voltammetry. In contrast, when more cathodic potentials were reached (formation of the dianion or beyond, reduction of the olefin) electrogenerated bases caused D-H exchange and might restore **3aH** progressively at the electrode interface: the specific cathodic step assigned to the reversible reduction of the latter sulfone (at a slightly more negative potential than the one corresponding to **3aD**) permits verification of the small but obvious difference between these two analogues. Lastly, exhaustive cathodic reductions carried out with both **3H** and **3D** in DMSO + 5% D_2O led exclusively to the same mixture of deuteriodimers.

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