Electrochemical behaviour of aromatic polysulfones

II Cathodic reduction of *o*-bis(alkylsulfonyl)benzenes in aprotic media in the presence of aliphatic halides

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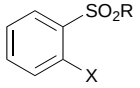
o-Bis(alkylsulfonyl)benzenes taken as disulfonylbenzene model substrates lead unexpectedly, under cathodic reduction performed in aprotic media in the presence of an excess of alkyl halide, to an alkylation concomitantly with a monocleavage reaction. The formation mechanism of these alkylated aromatic monosulfones is discussed on the basis of an electron-transfer reaction between the sulfone anion radical and the organic halide followed by a radical coupling.

Comportement électrochimique des polysulfones aromatiques. II. Réduction cathodique des *o*-bis(alkylsulfonyl)benzènes en milieu aprotique en présence d'halogénures aliphatiques. Les *o*-bis(alkylsulfonyl) benzènes pris comme substrats modèles des disulfonylbenzènes conduisent, de façon inattendue, lors de leur réduction cathodique en milieu aprotique en présence d'un excès d'halogénure d'alkyle, à une alkylation concomitante à la réaction de monoclivage. Le mécanisme de formation de ces monosulfones aromatiques alkylées, basé sur une réaction de transfert d'électron entre le radical anion de la sulfone et l'halogénure organique suivi par un couplage radicalaire, est discuté.

Generally, it can be admitted that the sulfonyl group allows some strongly activating properties to be introduced into a given molecular structure.[1,2] The interest of sulfone chemistry appears to be reinforced owing to the ability of the arylsulfonyl moiety to be easily introduced and cleaved[3,4] afterwards. Thus, the sulfone function allows polarity inversion (*umpolung*).

The deprotection chemistry necessarily includes the cleavage of the right C—S bond for sulfones. Desulfonylation reactions can be carried out using different methods. Let us quote mild cleavage methods such as hydrogenolysis by means of Raney nickel,[5] sodium amalgam,[6] as well as alkali metals in amines.[7] As a matter of fact, reduction by sodium amalgam in protic media of a phenyl alkyl sulfone led to the alkane and phenylsulfinate.

Data relative to the cathodic reduction of regular aromatic sulfones (**1**, X = H) are now numerous and well documented.[8–10] They all conclude that the sulfone transient radical anion is cleaved. Papers dealing with more elaborate and complex sulfones are much rarer. *o*-Disulfonylbenzenes, (**1**, X = SO_2R) appeared to be of special interest and resemble the disulfonamides and disulfinic esters already studied by Horner and Schmitt.[11] More particularly, the novelty of the work reported by Novi *et al.*,[12] which showed the catalytic conversion in the presence of a strong base of a disubstituted *o*-bis(alkylsulfonyl)benzene into a cyclic monosulfone, prompted us to test the general behaviour of sulfones **2** where the R substituents are now exclusively alkyl groups.



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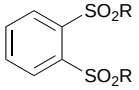


2

a R = Me
b R = Et
c R = Pr
d R = Bu
e R = Pentyl
f R = Hexyl
g R = Octyl

The work reported here aims to demonstrate the unexpected reactivity of sulfones **2a**–**g**, where besides the expected cleavage reaction, a possible radical coupling implying R$^{\cdot}$ could be taken into account in the reduction process. In the present full paper, and similarly to the work already reported[13] concerning a complete series of *o*-disulfones, classic experimental conditions were chosen: aprotic dipolar solvents, essentially dimethylformamide (DMF) as it is known not to be a strong H-atom donor solvent, quaternary ammonium salts as the electrolyte and a mercury pool cathode.

Results

Voltammetry

Linear sweep voltammetry achieved with the whole **2** series at slow sweep rate (v) exhibited a first reversible step within the range of −1.0 V to −1.5 V *vs.* the Ag/AgI/0.1 M I^- system, followed by two other steps (see Fig. 1). Voltammetric data concerning the two main steps are gathered in Table 1.

Coulometry

Coulometry experiments were performed to determine accurately the number of electrons involved in the overall electrochemical process (see Table 2). For a total consumption of the starting material an electricity amount between 1.25 and 1.65 moles of electrons per mole of sulfone appeared to be necessary. In Fig. 2, it can be seen that micropotentiostatic electrolysis at a small area mercury pool cathode did not bring about the disappearance of the second and the third step. The *in situ* addition of methyl iodide—currently used in sulfone chemistry to trap a possible sulfinic anion issued from the two-electron cleavage of the relevant sulfone—led to the emergence of a reversible step that strongly resembles that of the starting material. However, its current intensity is less than half of that already observed with **2** before the coulometry experiments. It is noticeable that step 2 also increased after the methylation process.

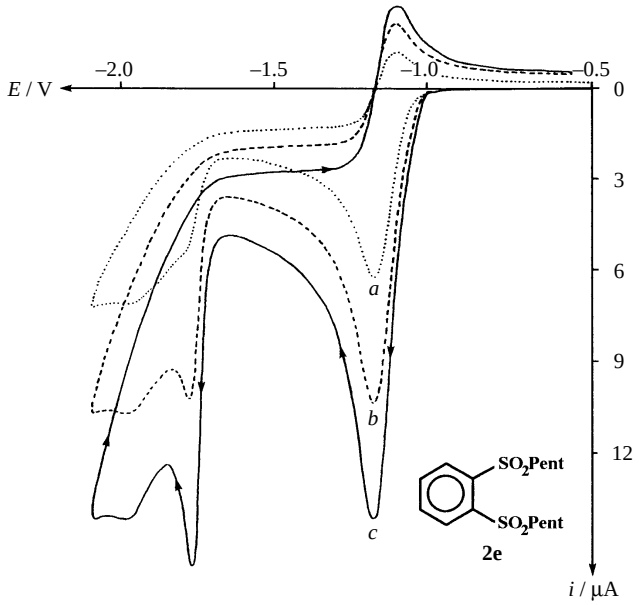


Fig. 1 Cyclic voltammetry of **2e** at various concentrations in DMF–0.1 M Bu_4NBF_4. Stationary mercury microelectrode (area 0.8 mm^2). Reference system: Ag/AgI/0.1 M I^-. Sweep rate: $v = 100$ mV s^{-1}. *a*: $C = 2.41 \times 10^{-3}$ M, *b*: $C = 3.85 \times 10^{-3}$ M, *c*: $C = 5.29 \times 10^{-3}$ M

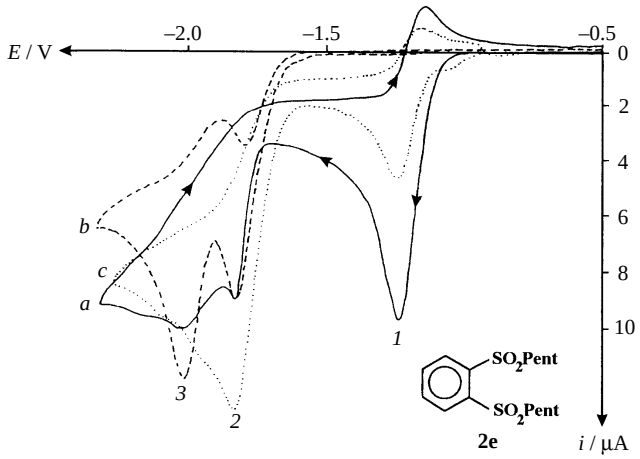


Fig. 2 Cyclic voltammetry of **2e** in DMF–0.1 M Bu_4NBF_4. Stationary mercury microelectrode (area 0.8 mm^2). Reference system: Ag/AgI/0.1 M I^{-1}. Sweep rate: $v = 100$ mV s^{-1}. *a*: $C = 4.8 \times 10^{-3}$ M, *b*: solution *a* after coulometry at -1.19 V until null current, *c*: solution *b* after addition of an excess of methyl iodide

Macroelectrolysis

All macroelectrolyses, performed on the entire **2** series at a stirred mercury pool cathode, afforded only four major products, as shown in Scheme 1. Data concerning the macroreductions of **2** are gathered in Table 2. In all cases, compounds **3** were produced in larger amounts than **4**. Yields of **5** (or at least that of the corresponding methyl sulfone by means of methyl iodide during the work-up) were generally found to be roughly equivalent to the sum of the yields of **3** and **4**. Totally cleaved compounds **6** could be considered as minor side products. Their relative yields were less than 15% in most cases.

Table 1 Features of the cyclic voltammetric response with disulfones **2**[a]

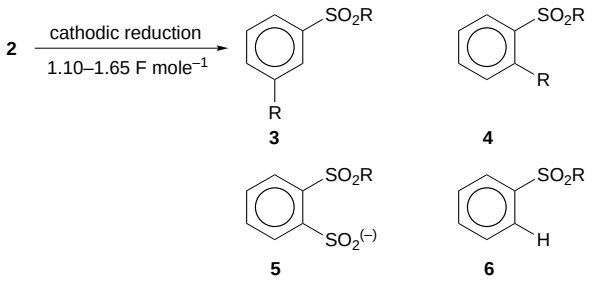
			First step		Second step	
Substrate	Concentration /10^3 M	$E°$/V[b]	E_{p_1}/V	i_1/μA	E_{p_2}/V	i_2/μA
2a	4.3	−1.30	−1.33	9.5	−1.89	7.1
2b	4.8	−1.12	−1.15	7.6	−1.70	7.4
2c	4.92	−1.14	−1.17	9.1	−1.76	7.5
2d	4.0	−1.13	−1.16	5.3	−1.72	5.1
2e	4.62	−1.15	−1.18	8.5	−1.75	7.8
2f	4.28	−1.15	−1.18	8.2	−1.77	6.0
2g	4.70	−1.19	−1.22	8.6	−1.78	6.8

[a] Stationary mercury microelectrode (area 0.8 mm^2). Electrolyte: DMF + 0.1 M Bu_4NBF_4 Reference system: Ag/AgI/0.1 M I^-. Sweep rate: 0.1 V s^{-1}. [b] Standard potential relative to the first electron transfer in DMF.

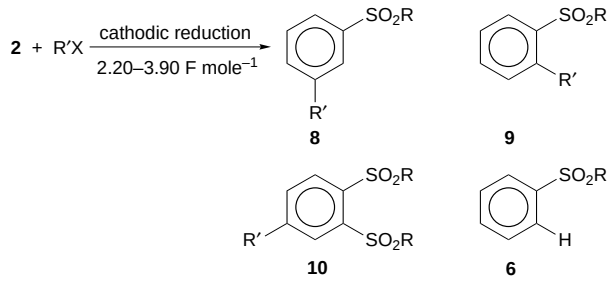
Table 2 Macroelectrolysis of disulfones **2** at a stirred mercury pool cathode[a]

					Isolated yields/%			
Entry	Substrate **2**[b]	Fixed potential /V	*n*/ F mol^{-1}	Solvent	**3**	**4**	**5**[c]	**6**
1	**2a**[d]	−1.32	1.42	aprotic DMF	<1	–	75	10
2	**2a**[e]	−1.32	1.25	aprotic DMF	15	4	20	12
3	**2b**	−1.18	1.34	aprotic DMF	33	2	30	13
4	**2b**	−1.18	1.12	DMF + $PhSNBu_4$ [f]	42	<1	—	—
5	**2b**	−1.18	1.45	DMF + Phenol[g]	22	2	28	28
6	**2c**	−1.20	1.40	aprotic DMF	30	2	30	12
7	**2d**	−1.21	1.31	aprotic DMF	32	2	34	11
8	**2d**	−1.21	1.10	DMF + $AcONBu_4$ [h]	44	<1	—	—
9	**2e**	−1.19	1.65	aprotic DMF	32	2	30	10
10	**2f**	−1.17	1.52	aprotic DMF	34	4	33	7

[a] Electrode area: 10 cm^2. Solvent: DMF or DMSO containing 0.1 M Bu_4NBF_4. Potentials are referred to the Ag/Ag I/0.1 M I^-system in DMF. [b] Concentration of 10^{-2} mol l^{-1} except as noted. [c] Sulfinate was alkylated with methyl iodide in excess added directly to the catholyte. Yields reported in this column are those relevant to the obtained disulfone. [d] Concentration of 8.6×10^{-3} mol l^{-1}. [e] Concentration of 2.2×10^{-2} mol l^{-1}. [f] Molar excess factor towards **2b** is 20. [g] Molar excess factor towards **2b** is 4. [h] Molar excess factor towards **2d** is 6.



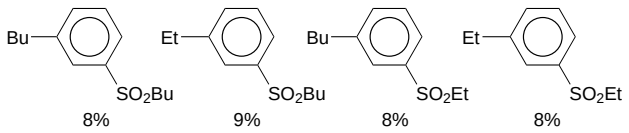
Scheme 1



Scheme 2

Mixed electrolysis of two different disulfones

A mixture of **2b** and **2d** in equal amounts in the catholyte ($C = 1.2 \times 10^{-2}$ M) was electrolysed at −1.2 V and consumed 1.4 moles of electrons per total sulfone amount. A mixture of four main compounds in more or less equal proportions could be isolated:



Reduction of 2 in the presence of alkyl halides

Preliminary experiments[13d] demonstrated that disulfones **2** also led to the alkylation products **8** and **9** in high yields when reduced in the presence of alkyl halides (R′X) in large excess. The chosen R′X were not electrochemically reduced prior to the disulfones. Alkylation in the *meta* position was found to be strongly favored. A minor *ortho*-alkylation reaction was concomitantly observed. Here, in most of the cases, the yield for the overall alkylation was quite high (at least 70–80% of isolated compounds). Under these experimental conditions (large excess of R′X), cleavage of disulfones leading to sulfinate **5** was not observed (see Table 3) with nonbulky R′ groups. Additionally, it is worth mentioning that greater electricity consumptions are readily consistent with a homogeneous indirect reduction of the alkyl halide by the **2** anion radical.

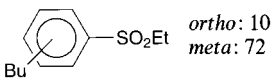
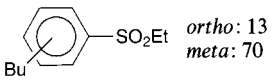
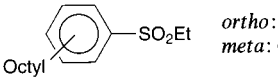
The scope of this study has been extended to a large palette of primary and secondary alkyl halides as reported in Table 4 and all results are approximately the same. However, when the alkyl group R′ was particularly bulky (like Bu^tCH_2), the alkylation yield dropped drastically and self-alkylation with the alkyl group R of the disulfone, then yielding **3** and **4**, became predominant. Secondary products (such as **10**, see Scheme 2) were also isolated (see Table 4, entries 1, 3 and 5).

Alkyl α,ω-dihalides have also been used as alkylating agents in these experiments. Such compounds might have been expected to undergo a second coupling, either intramolecularly to yield bicyclic derivatives or by reacting with another disulfone. Such reactions were absolutely not observed and monoalkylations remained the only reaction pathways (see Table 5, entries 2–6).

Additional important information about the alkylation mechanism could be obtained from the selectivity observed in the case of an optically active halide. The inversion-to-racemization ratio for the reaction between aromatic radical anions and chiral alkyl halides has been discussed in terms of a competition between a classical S_N2 pathway (leading to complete configuration inversion) and an electron transfer followed by a coupling between the alkyl radical and the aromatic anion radical.[14] In our case (see Table 5, entry 1), a total racemization occurred, ruling out the S_N2-type reaction.

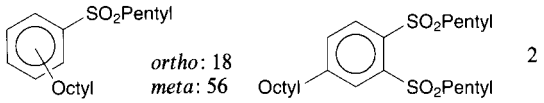
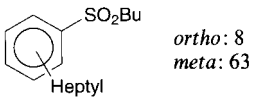
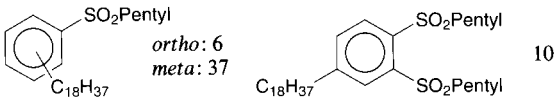
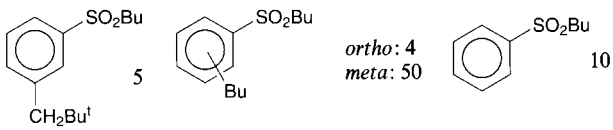
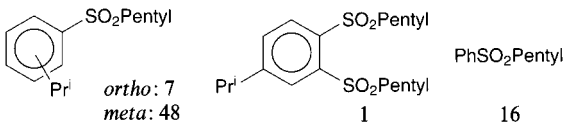
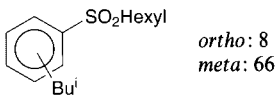
Hexen-5-en-1-yl radical was first reported in 1963 to undergo an intramolecular ring closure leading to the cyclopentylmethyl radical.[15] Since then, this species and its derivatives, often referred to as radical probes or radical clocks, have gained widespread acceptance as mechanistic tools to provide evidence of the radical character of substitution reactions.[16] ω-Bromoalk-1-enes, potential precursors of ω-alk-1-enyl radicals, behaved similarly to alkyl halides when they were added during the electrochemical reduction of disulfones **2**: when added in excess in cyclic voltammetry, they induced the loss of reversibility of the disulfone peaks without noticeable increase of current, and preparative scale electrolyses yielded *meta*- and *ortho*-alkylated sulfones of type **8** and **9** (see Table 5, entry 7). It is also worth noting that the cyclized derivative **12** was not obtained in this experiment, as well as in similar ones[13c] not reported in the present paper.

Table 3 Electrolysis of **2b** in the presence of some R′X compounds[a]

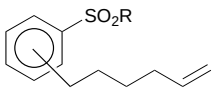
Substrate	R′X	γ[b]	n/F mol^{-1}	Isolated electrolysis products/%
2b	BuBr	20	4.1	 *ortho*: 10 *meta*: 72
2b	BuI	5	4.3	 *ortho*: 13 *meta*: 70
2b	Octyl-I	3	3.3	 *ortho*: 8 *meta*: 64

[a] Solvent: DMF containing 0.1 M Bu_4NBF_4. Cathode: stirred mercury pool (area 10 cm^2). Substrate concentration at the start of the electrolysis: 1.2×10^{-2} M. Applied voltage: −1.20 V. [b] Excess factor (molar ratio [R′X]/[**2**]).

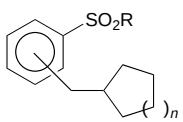
Table 4 Macroelectrolysis of various disulfones **2** in the presence of alkyl halides at a stirred mercury pool cathode[a]

Entry	Substrate **2**	Alkyl halide R′X (γ^b)	Fixed potential/V	n/ F mol^{-1}	Isolated yields/%
1	**2e**	Octyl-I (3)	−1.20	2.8	 2
2	**2d**	Heptyl-Br (16)	−1.25	2.2	
3	**2e**	$C_{18}H_{37}Br$ (8)	−1.30	2.5	 10
4	**2d**	Bu^tCH_2Br (20)	−1.30	2.0	 5 10
5	**2e**	Pr^iBr (10)	−1.20	2.3	 1 16
6	**2f**	Bu^iBr (4)	−1.28	2.5	

[a] Electrode area: 10 cm^2. Solvent: DMF containing 0.1 M Bu_4NBF_4. Potentials are referred to the Ag/AgI/0.1 M I^- system in DMF. [b] Molar excess factor towards **2**.



8, 9



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Discussion

The cathodic decomposition of disulfones **2** appears to be an alkylation reaction concomitant with a cleavage reaction, leading to a global scheme that is really unexpected. Kinetic studies[13c] in UV-visible spectroscopy that followed the concentration decay of the anion radical of **2** *in solution* have demonstrated that this decomposition obeys a second-order kinetic law, likely with a charge-transfer complex between the anion radical and the substrate prior to decomposition.

In contrast, when the reduction of disulfones **2** was performed in the presence of alkyl halides, the global mechanism seems to fit quite well with previously reported results[17] concerning the indirect reduction of alkyl halides (RX) in the case of homogeneous electron transfer (ET) by means of the anion radical of the mediator (A). Thus, the reaction scheme below describes a nondissociative ET but dissociative ET can also be taken into account.

$$A \underset{}{\overset{e^-}{\rightleftharpoons}} A^{\bullet -}$$

$$A^{\bullet -} + RX \rightleftharpoons A + [RX]^{\bullet -}$$

$$[RX]^{\bullet -} \xrightarrow{k_C} R^{\bullet} + X^-$$

A radical R$^{\bullet}$ can be formed *in solution* and then further couple with the mediator anion radical in the general case.

$$R^{\bullet} + A^{\bullet -} \rightarrow AR^-$$

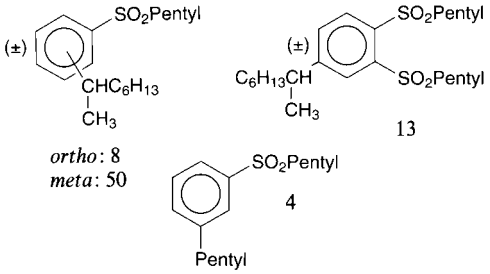
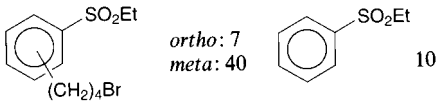
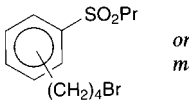
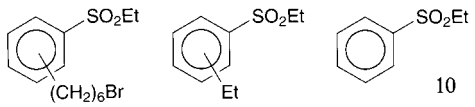
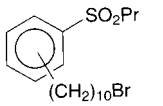
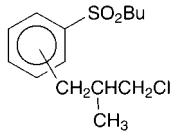
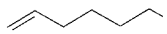
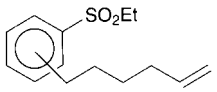
In the present case, R$^{\bullet}$ issued from the cathodic cleavage of **2**$^{\bullet -}$ can couple with **2**$^{\bullet -}$. The mechanism is obviously rendered more complex since **2** intrinsically possesses two potential leaving groups.

$$\mathbf{2}^{\bullet -} + R^{\bullet} \longrightarrow [\mathbf{2}{-}R]^- \longrightarrow \mathbf{3} + \mathbf{4}$$

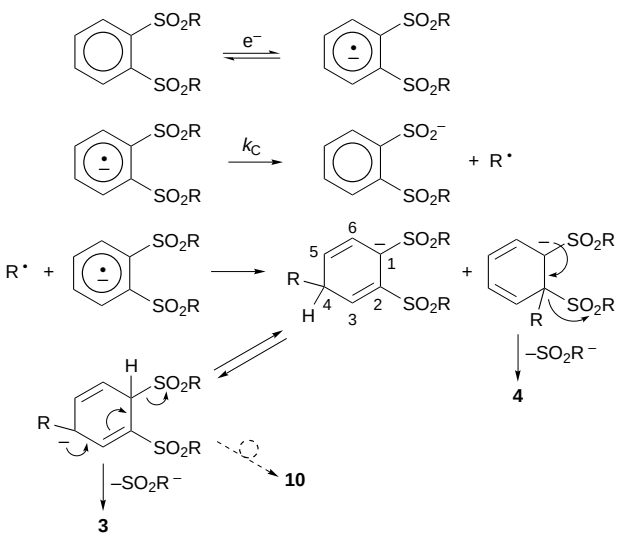
Tentatively, a general mechanism can be proposed (see Scheme 3). It takes into account the fact that the alkylation cannot be intramolecular as shown by the results of mixed electrolyses (example described with 2b + 2d), which are in full agreement with the statistical coupling of four radical species leading to four dimers in equal amounts.

Therefore, the 'self-alkylation' observed in the decomposition of **2** under electron transfer (the total alkylation yield cannot exceed 50% owing to formation of the sulfinate **5**) can also be achieved with success in the presence of an excess of alkyl halide R′X (obviously R′ can be equal to R). Thus, compounds **3** and **4** on the one hand and **8** and **9** on the other hand could be obtained but in much higher yields. With structure **2** only two sites seem to be suitable to yield a radical coupling: the *ipso*-type coupling may explain, owing to the bulkiness of the sulfonyl group, the much lower amount of final *ortho*-substituted compounds **4** and **9** than those observed with the *meta*-substituted compounds **3** and **8**. With neopentyl bromide, only the *meta* derivative could be obtained (Table 4, entry 4), suggesting (which is reasonable) that the neopentyl radical could not reach the carbon bearing

Table 5 Macroelectrolysis of disulfones **2** in the presence of alkyl halides or dihalides at a stirred mercury pool cathode[a]

Entry	Substrate **2**	Alkyl halide R′X (γ^b)	Fixed potential/V	n/F mol^{-1}	Isolated yields/%
1	**2e**	(*R*)-$C_6H_{13}CH^*(CH_3)Br$ (2)	−1.20	2.3	 *ortho*: 8 *meta*: 50 13 4
2	**2b**	$Br(CH_2)_4Br$ (4)	−1.15	3.9	 *ortho*: 7 *meta*: 40 10
3	**2c**	$Br(CH_2)_4Br$ (16)	−1.15	2.3	 *ortho*: 8 *meta*: 56
4	**2b**	$Br(CH_2)_6Br$ (8)	−1.18	1.7	 *ortho*: 6 *meta*: 31 *ortho*: 4 *meta*: 13 10
5	**2c**	$Br(CH_2)_{10}Br$ (10)	−1.20	3.3	 *ortho*: 10 *meta*: 65
6	**2d**	(±)-$BrCH_2CH(CH_3)CH_2Cl$ (8)	−1.20	3.7	 *ortho*: 11 *meta*: 60
7	**2b**	 (20)	−1.25	2.8	 *ortho*: 11 *meta*: 60

[a] Electrode area: 10 cm^2. Solvent: DMF containing 0.1 M Bu_4NBF_4. Potentials are referred to the Ag/AgI/0.1 M I^- system in DMF. [b] Molar excess factor towards **2**.



Scheme 3

a sulfonyl moiety. In this case, the coupling is anyway so slow that the regular decomposition of **2** may occur.

Optically active R′X (Table 5, entry 1) allowed us to check the radical-coupling nature of the key reaction[14] since 100% racemization was observed. Similarly (entry 7), the use of radical probes[15,16] did not allow any cyclization of the expected hex-5-enyl primary free radical to be seen. This suggests a very fast deactivation by coupling of this radical. Unexpectedly, entries 2–6 (Table 5) relative to the use of α,ω-dibromoalkanes as R′X demonstrated the impossibility of getting twinned alkylation reactions.

All these previous results could suggest the existence of an intermediary complex between $\mathbf{2}^{\bullet -}$ and R′X [the existence of which was confirmed by the disappearance of reversibility in the CV of **2** when R′X (see Fig. 3) was added, although no current increase was observed[13d]]. Under these conditions, the alkylation process could occur essentially inside a solvent cage:

$$\mathbf{2}^{\bullet -} + R'X \rightleftharpoons [\mathbf{2}, R'X]^{\bullet -} \longrightarrow [\mathbf{2}, R'^{\bullet}] \xrightarrow[\text{fast}]{\mathbf{2}^{\bullet -}} \mathbf{2}{-}R'^{-} + \mathbf{2}$$

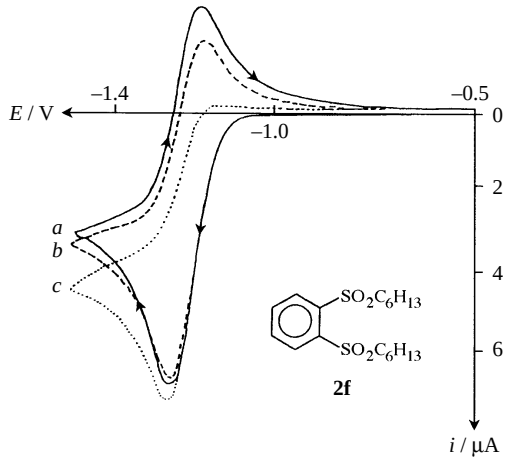


Fig. 3 Cyclic voltammetry of **2f** in DMF–0.1 M Bu_4NBF_4. Stationary mercury microelectrode (area 0.8 mm^2). Reference system: Ag/AgI/0.1 M I^-. Sweep rate: $v = 100$ m V s^{-1}. Curve morphology in the presence of increasing concentration of R′X = Pr^i Br with γ the molar excess factor toward **2f**. *a* γ = 0, *b* γ = 2, *c* γ = 20

Lastly, the general formation, besides **8** and **9**, of compounds **10** (see Table 4, entries 1, 3 and 5) appears fully compatible with the main coupling in the 4 position between $\mathbf{2}^{\bullet -}$ and R″ (see Scheme 3). Under these conditions, the anion is protonated and readily rearomatized during the work-up.

Experimental

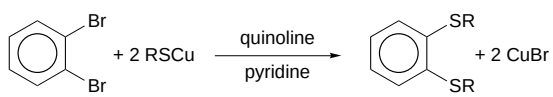
The products were identified mainly by 60 MHz (Varian EM 360 A), 200 MHz (Bruker ARX 200) or 300 MHz (Bruker AC 300 P) ^{1}H NMR and by high resolution mass spectrometry (Varian MAT 311 at the Centre de Mesures Physiques de l'Ouest, Université de Rennes 1). In the cases where an additional structural proof was essential, ^{13}C NMR (75 MHz) spectra were obtained and/or selective irradiation performed. All the NMR spectra were recorded in $CDCl_3$ with TMS as an internal reference. Details on the determination of the alkylation position in compounds **3** and **4** have already been reported.[13d]

Syntheses of disulfones 2

Several modes of synthesis could be used to get the whole **2** series; the oxidation of the corresponding dithioethers either by a solution (30%) of hydrogen peroxide in acetic acid[18] or by using the method of Trost and Curran[19] (50% oxone solution in methanol) was chosen. Most of the dithioethers were known and have been prepared according to the following procedure.[20] The first step consists of forming cuprous salts from the chosen thiols:

$$2\ RSH + Cu_2O \rightarrow 2\ RSCu + H_2O$$

followed by the second synthesis step corresponding to the substitution of *o*-dibromobenzene to lead to the dithioethers as key products:



However, with disulfone **2a**, the use of another method appeared necessary: 1,2-benzenedithiol was alkylated with methyl iodide to yield the corresponding dithioether, as previously described.[18c,21]

Physical constants of compound **2a**[22] have been reported. Those of the unknown disulfones **2** are detailed below:

2b: mp: 123–125 °C. MS: exact mass measurement: obsd, 262.0333; calcd for $C_{10}H_{14}O_4S_2$, 262.0333. 200 MHz ^{1}H NMR δ: 1.29 (6H, t, $J = 7.5$ Hz); 3.69 (4H, q, $J = 7.5$ Hz); 7.83–7.94 (2H, m) and 8.26–8.38 (2H, m).

2c: mp: 107–108 °C. 200 MHz ^{1}H NMR δ: 1.03 (6H, t, $J = 7.4$ Hz); 1.77 (4H, tq, $J = 7.4$ and 7.9 Hz); 3.65 (4H, t, $J = 7.9$ Hz); 7.86–8.02 (2H, m); 8.27–8.42 (2H, m).

2d: mp: 86–87 °C. MS: exact mass measurement: obsd, 318.1108; calcd for $C_{14}H_{22}O_4S_2$, 318.0960. 200 MHz ^{1}H NMR δ: 0.90 (6H, m, $J = 7.2$ Hz); 1.42 (4H, tq, $J = 6.9$ and 7.2 Hz); 1.70 (4H, tt, $J = 6.9$ and 8.0 Hz); 3.65 (4H, t, $J = 8.0$ Hz); 7.80–7.92 (2H, m); 8.25–8.37 (2H, m).

2e: mp: 69–70 °C. MS: exact mass measurement: obsd, 346.1266; calcd for $C_{16}H_{26}O_4S_2$, 346.1272. 300 MHz ^{1}H NMR δ: 0.88 (6H, t, $J = 7.0$ Hz); 1.25–1.42 (8H, m); 1.66–1.79 (4H, m); 3.63 (4H, t, $J = 8.0$ Hz); 7.81–7.91 (2H, m); 8.26–8.37 (2H, m).

2f: mp: 38–39 °C. MS: exact mass measurement: obsd, 374.1595; calcd for $C_{18}H_{30}O_4S_2$, 374.1585. 200 MHz ^{1}H NMR δ: 0.85 (6H, t, $J = 6.5$ Hz); 1.11–1.50 (12H, m); 1.60–1.82 (4H, m); 3.64 (4H, t, $J = 8.0$ Hz); 7.80–7.91 (2H, m); 8.25–8.37 (2H, m).

2g: liquid. MS: exact mass measurement: obsd, 430.2592; calcd for $C_{22}H_{38}O_4S_2$, 430.2212. 60 MHz ^{1}H NMR δ: 1.3 (30 H, m); 3.7 (4H, t); 7.9 (2H, m); 8.3 (2H, m).

Electrolyses

All the electrolyses were achieved with a large H-shaped cell (total volume: 150 mL) equipped with a G4 glass frit separator. The stirred mercury pool cathode potential was controlled with an EGG potentiostat Model 173. The reference electrode was in all cases an Ag/AgI/0.1 M $INBu_4$ system in DMF. The counter electrode was always a glassy carbon plate (total area: about 15 cm^2). An argon atmosphere was maintained over the electrolysis solution in all cases. Amounts of disulfones **2** electrolysed until null current were of the order of 200 to 300 mg. An alkyl halide R′X could be (or not) added in the cathode compartment. Excess factors (γ) as described in Tables 3 and 4 aim to quantify the relative amount of alkylating reagents. After electrolysis completion, the entire contents of the cathodic compartment were poured into 150 mL of distilled water. The resulting solution was extracted with diethyl ether. The ethereal phase was then washed twice with water and dried over magnesium sulfate. After evaporation under vacuum, the dried extract was separated by column chromatography (silica gel, eluent: ethyl acetate–pentane).

Electrolysis products

Electrolysis of 2a. Compound **3a** was identified as *m*-tolyl methyl sulfone by comparison of the NMR data with those reported in the literature.[23]

Compound **4a** was identified as *o*-tolyl methyl sulfone by comparison of the NMR data with those reported in the literature.[23,24]

Compound **5a**: In order to avoid confusion with the starting compound, sulfinate was trapped with ethyl iodide. It has been checked that addition of methyl iodide to the electrolysis mixture yielded **2a**. **5a** was identified as *o*-(methylsulfonyl)-phenyl ethyl sulfone by comparison of the NMR data with those reported in the literature.[25] Mp: 105–106 °C (lit.[25] 100–102 °C).

Compound **6a** was identified as methyl phenyl sulfone by comparison with an authentic sample.

Electrolysis of 2b. Compound **3b**: liquid. MS: exact mass measurement: obsd, 198.0721; calcd for $C_{10}H_{14}O_2S$, 198.0715. 200 MHz ^{1}H NMR δ: 1.28 (3H, t, $J = 7.6$ Hz); 1.28 (3H, t, $J = 7.5$ Hz); 2.75 (2H, q, $J = 7.6$ Hz); 3.10 (2H, q, $J = 7.5$ Hz);

7.40–7.53 (2H, m); 7.66–7.77 (m, 2H).

Compound **4b**: liquid. MS: exact mass measurement: obsd, 198.0702; calcd for $C_{10}H_{14}O_2S$, 198.0715. 200 MHz ^{1}H NMR δ: 1.30 (3H, t, J = 7.4 Hz); 1.33 (3H, t, J = 7.5 Hz); 3.06 (2H, q, J = 7.4 Hz); 3.17 (2H, q, J = 7.5 Hz); 7.33 (1H, ddd, ^3J = 7.7 and 7.7 Hz, ^4J = 1.7 Hz); 7.36 (1H, dd, ^3J = 7.6 Hz, ^4J = 1.7 Hz); 7.54 (1H, ddd, ^3J = 7.7 and 7.7 Hz, ^4J = 1.3 Hz); 7.98 (1H, dd, ^3J = 7.7 Hz, ^4J = 1.3 Hz).

Compound **5b** is the same as **5a** above.

Compound **6b** was identified as ethyl phenyl sulfone by comparison with an authentic sample.

Electrolysis of 2c. Compound **3c**: liquid. 60 MHz ^{1}H NMR δ: 0.8–1.2 (6H, m); 1.3–2.1 (m, 4H); 2.7 (2H, t); 3.1 (2H, t); 7.4–7.9 (4H, m).

Compound **4c**: liquid. 300 MHz ^{1}H NMR δ: 0.86–0.95 (6H, m); 1.5–1.8 (4H, m); 3.0 (2H, t, J = 8 Hz); 3.10 (2H, t, J = 8 Hz); 7.30–8.05 (4H, m).

Compound **5c**: mp: 86–87 °C. MS: exact mass measurement: obsd, 262.0333; calcd for $C_{10}H_{14}O_4S_2$, 262.0334. 60 MHz ^{1}H NMR δ: 1.2 (3H, t, J = 7.5 Hz); 1.8–1.9 (2H, m); 3.45 (3H, s); 3.65 (2H, t, J = 7.5 Hz); 8.0–8.5 (4H, m).

Compound **6c** was identified as propyl phenyl sulfone by comparison with an authentic sample.

Electrolysis of 2d. Compound **3d**: liquid. MS: exact mass measurement: obsd, 254.1340; calcd for $C_{14}H_{22}O_2S$, 254.1341. 200 MHz ^{1}H NMR δ: 0.89 (3H, t, J = 7.3 Hz); 0.93 (3H, t, J = 7.3 Hz); 1.37 (4H, m); 1.62 (m, 4H); 2.71 (2H, t, J = 7.5 Hz); 3.09 (2H, t, J = 8.0 Hz); 7.43–7.50 (2H, m); 7.65–7.77 (m, 2H).

Compound **4d**: liquid. 200 MHz ^{1}H NMR δ: 0.89 (3H, t, J = 7.3 Hz); 0.96 (3H, t, J = 7.3 Hz); 1.37 (4H, m); 1.63 (m, 4H); 2.70 (2H, t, J = 7.5 Hz); 3.10 (2H, t, J = 8.0 Hz); 7.35 (1H, ddd, ^3J = 7.7 and 7.7 Hz, ^4J = 1.7 Hz); 7.39 (1H, dd, ^3J = 7.7 Hz, ^4J = 1.7 Hz); 7.56 (1H, ddd, ^3J = 7.7 and 7.7 Hz, ^4J = 1.3 Hz); 7.99 (1H, dd, ^3J = 7.7 Hz, ^4J = 1.3 Hz).

Compound **5d**: mp: 72.5–75 °C.[18c] MS: exact mass measurement: obsd, 276.0864; calcd for $C_{11}H_{16}O_4S_2$, 276.0490. 60 MHz ^{1}H NMR δ: 1.2 (7H, m); 3.45 (3H, s); 3.6 (2H, t); 8.0 (4H, m).

Compound **6d** was identified as butyl phenyl sulfone by comparison with an authentic sample.

Electrolysis of 2e. Compound **3e**: liquid. MS: exact mass measurement: obsd, 282.1654; calcd for $C_{16}H_{26}O_2S$, 282.1654. 60 MHz ^{1}H NMR δ: 0.7–1.1 (6H, m); 1.2–2.0 (12H, m); 2.75 (2H, t); 3.15 (2H, t); 7.35–7.90 (4H, m).

Compound **4e**: liquid. MS: exact mass measurement: obsd, 282.1654; calcd for $C_{16}H_{26}O_2S$, 282.1654. 300 MHz ^{1}H NMR δ: 0.82–0.94 (6H, m); 1.22–1.43 (m, 8H); 1.62–1.79 (m, 4H); 3.0 (t, 2H, J = 8.0 Hz); 3.11 (t, 2H, J = 8.0 Hz); 7.3–8.02 (m, 4H).

Compound **5e**: liquid. MS: exact mass measurement: obsd, 290.1182; calcd for $C_{12}H_{18}O_4S_2$, 290.0647. 60 MHz ^{1}H NMR δ: 1.15 (9H, m); 3.45 (3H, s); 3.65 (2H, t); 7.8–8.2 (4H, m).

Compound **6e** was identified as pentyl phenyl sulfone by comparison with an authentic sample.

Electrolysis of 2f. Compound **3f**: liquid. MS: exact mass measurement: obsd, 310.1975; calcd for $C_{18}H_{30}O_2S$, 310.1967. 300 MHz ^{1}H NMR δ: 0.85 (3H, t, J = 6.9 Hz); 0.88 (3H, t, J = 6.8 Hz); 1.17–1.42 (12H, m); 1.56–1.77 (4H, m); 2.69 (2H, t, J = 7.7 Hz); 3.07 (2H, t, J = 8.0 Hz); 7.42–7.50 (2H, m); 7.67–7.75 (2H, m). 75 MHz ^{13}C NMR δ: 13.91; 14.05; 22.29; 22.56; 22.62; 27.96; 28.84; 31.18 (2C); 31.61; 35.73; 56.37; 125.35; 127.74; 129.14; 133.74; 139.13; 133.58.

Compound **4f**: liquid. MS: exact mass measurement: obsd, 310.1975; calcd for $C_{18}H_{30}O_2S$, 310.1967. 300 MHz ^{1}H NMR δ: 0.85 (3H, t, J = 6.8 Hz); 0.89 (3H, t, J = 7.0 Hz); 1.16–1.49 (12H, m); 1.59–1.77 (4H, m); 3.00 (2H, t, J = 8.0 Hz); 3.11 (2H, t, J = 8.0 Hz); 7.36 (1H, ddd, ^3J = 7.7 and 7.9 Hz; ^4J = 1.4 Hz); 7.38 (1H, dd, ^3J = 7.7 Hz, ^4J = 1.4 Hz); 7.54 (1H, ddd, ^3J = 7.7 and 7.7 Hz, ^4J = 1.3 Hz); 7.98 (1H, dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz).

Compound **5f**: liquid. 60 MHz ^{1}H NMR δ: 1.15 (11H, m); 3.50 (3H, s); 3.75 (2H, t); 8.0–8.3 (4H, m).

Compound **6f** was identified as hexyl phenyl sulfone by comparison with an authentic sample.

Electrolysis of 2g. Compound **3g**: liquid. MS: exact mass measurement: obsd, 366.2602; calcd for $C_{22}H_{38}O_2S$, 366.2593. 60 MHz ^{1}H NMR δ: 1.30 (30H, m); 2.90 (4H, m); 7.60 (4H, m).

Compound **5g** was identified as *o*-(methylsulfonyl)phenyl octyl sulfone by comparison of the NMR data with those reported in the literature.[26]

Compound **6g** was identified as octyl phenyl sulfone by comparison with an authentic sample.

Electrolysis of 2e in the presence of octyl iodide. Compound **8e** (R′ = octyl): liquid. MS: exact mass measurement: obsd, 324.2129; calcd for $C_{19}H_{32}O_2S$, 324.2123. 300 MHz ^{1}H NMR δ: 0.86 (3H, t, J = 7.1 Hz); 0.88 (3H, t, J = 6.3 Hz); 1.19–1.40 (14H, m); 1.58–1.78 (4H, m); 2.69 (2H, t, J = 7.7 Hz); 3.07 (2H, t, J = 8.1 Hz); 7.40–7.52 (2H, m); 7.66–7.77 (2H, m). 75 MHz ^{13}C NMR δ: 13.68; 14.08; 22.11; 22.33; 22.66; 29.21 (3C); 30.38; 31.20; 31.85; 35.74; 56.34; 125.35; 127.74; 129.14; 133.74; 139.15; 144.58.

Compound **9e** (R′ = octyl): liquid. MS: exact mass measurement: obsd, 324.2129; calcd for $C_{19}H_{32}O_2S$, 324.2123. 200 MHz ^{1}H NMR δ: 0.86 (3H, t, J = 6.9 Hz); 0.88 (3H, t, J = 6.5 Hz); 1.15–1.44 (14H, m); 1.54–1.80 (4H, m); 3.00 (2H, t, J = 7.7 Hz); 3.11 (2H, t, J = 8.0 Hz); 7.36 (1H, ddd, ^3J = 7.6 and 8.1 Hz, ^4J = 1.3 Hz); 7.38 (1H, dd, ^3J = 7.6 Hz, ^4J = 1.3 Hz); 7.51 (1H, ddd, ^3J = 7.6 and 7.6 Hz, ^4J = 1.5 Hz), 7.98 (1H, dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz). 50 MHz ^{13}C NMR δ: 13.70; 14.10; 22.12; 22.19; 22.67; 29.25; 29.46; 29.80; 30.43; 31.87; 32.24; 33.06; 56.43; 126.34; 130.37; 131.60; 133.46; 137.02; 143.22.

Compound **10e** (R′ = octyl): liquid. 300 MHz ^{1}H NMR δ: 0.84 (3H, t, J = 6.8 Hz); 0.88 (6H, t, J = 6.8 Hz); 1.15–1.47 (18H, m); 1.51–1.78 (6H, m); 2.79 (2H, t, J = 7.6 Hz); 3.56–3.68 (4H, m); 7.61 (1H, dd, ^3J = 8.0 Hz, ^4J = 1.8 Hz); 8.09 (1H, d, ^4J = 1.8 Hz); 8.19 (1H, d, ^3J = 8.0 Hz).

Electrolysis of 2d in the presence of heptyl bromide. Compound **8d** (R′ = heptyl): liquid. 300 MHz ^{1}H NMR δ: 0.88 (3H, t, J = 6.9 Hz); 0.89 (3H, t, J = 7.3 Hz); 1.19–1.50 (10H, m); 1.58–1.75 (4H, m); 3.08 (2H, t, J = 8.0 Hz); 3.32 (2H, t, J = 7.7 Hz); 7.67–7.75 (2H, m); 7.43–7.51 (2H, m). 75 MHz ^{13}C NMR δ: 13.50; 14.07; 21.56; 22.63; 24.65; 29.07; 29.14; 31.19; 31.76; 35.73; 56.13; 125.36; 127.74; 129.14; 133.74; 139.15; 144.59.

Compound **9d** (R′ = heptyl): liquid. 300 MHz ^{1}H NMR δ: 0.88 (3H, t, J = 6.8 Hz); 0.89 (3H, t, J = 7.3 Hz); 1.20–1.51 (10H, m); 1.57–1.80 (4H, m); 3.00 (2H, t, J = 8.0 Hz); 3.12 (2H, t, J = 8.1 Hz); 7.36 (1H, ddd, ^3J = 7.5 and 7.9 Hz, ^4J = 1.3 Hz); 7.38 (1H, dd, ^3J = 7.5 Hz, ^4J = 1.3 Hz); 7.54 (1H, ddd, ^3J = 7.5 and 7.5 Hz, ^4J = 1.4 Hz), 7.98 (1H, dd, ^3J = 7.9 Hz, ^4J = 1.3 Hz). 75 MHz ^{13}C NMR δ: 13.68; 14.08; 22.11; 22.33; 22.66; 29.21; 30.38; 31.20; 31.85; 35.74; 56.34; 125.35; 127.74; 129.14; 133.74; 139.15; 144.58.

Electrolysis of 2e in the presence of octadecyl bromide. Compound **8e** (R′ = $C_{18}H_{37}$): liquid. MS: exact mass measurement: obsd, 464.3684; calcd for $C_{29}H_{52}O_2S$, 464.3688. 300 MHz ^{1}H NMR δ: 0.86 (3H, t, J = 7.0 Hz); 0.88 (3H, t, J = 6.7 Hz); 1.12–1.50 (36H, m); 1.57–1.78 (4H, m); 2.69 (2H, t, J = 7.7 Hz); 3.07 (2H, t, J = 8.1 Hz); 7.42–7.50 (2H, m); 7.67–7.75 (2H, m). 75 MHz ^{13}C NMR δ: 13.69; 14.12; 22.11; 22.33;

22.70; 29.21; 29.38; 29.44; 29.58; 29.68 (3C); 29.72 (6C); 30.38; 31.21; 31.95; 35.74; 56.74; 125.34; 127.74; 129.13; 133.73; 139.15; 144.58.

Compound **9e** ($R' = C_{18}H_{37}$): liquid. 200 MHz ^{1}H NMR δ: 0.86 (3H, t, $J = 6.8$ Hz); 0.89 (3H, t, $J = 6.8$ Hz); 1.13–1.39 (36H, m); 1.53–1.79 (4H, m); 3.00 (2H, t, $J = 8.1$ Hz); 3.07 (2H, t, $J = 8.0$ Hz); 7.36 (1H, ddd, $^3J = 7.5$ and 7.9 Hz, $^4J = 1.4$ Hz); 7.38 (1H, dd, $^3J = 7.5$ Hz, $^4J = 1.4$ Hz); 7.51 (1H, ddd, $^3J = 7.5$ and 7.5 Hz, $^4J = 1.7$ Hz), 7.98 (1H, dd, $^3J = 7.9$ Hz, $^4J = 1.7$ Hz).

Compound **10e** ($R' = C_{18}H_{37}$): liquid. MS: exact mass measurement: obsd, 598.4106; calcd for $C_{34}H_{63}O_4S_2$, 598.4089. 200 MHz ^{1}H NMR δ: 0.86 (3H, t, $J = 6.8$ Hz); 0.89 (6H, t, $J = 6.8$ Hz); 1.13–1.39 (38H, m); 1.53–1.79 (6H, m); 2.78 (2H, t, $J = 7.6$ Hz); 3.61 (2H, t, $J = 7.8$ Hz); 3.63 (2H, t, $J = 7.8$ Hz); 7.60 (1H, dd, $^3J = 8.0$ Hz, $^4J = 1.8$ Hz); 8.08 (1H, d, $^4J = 1.6$ Hz); 8.18 (1H, d, $^3J = 8.0$ Hz).

Electrolysis of 2d in the presence of neopentyl bromide. Compound **8d** ($R' = CH_2Bu^t$): liquid. 200 MHz ^{1}H NMR δ: 0.88 (3H, t, $J = 7.2$ Hz); 0.91 (9H, s); 1.22–1.52 (2H, m); 1.54–1.78 (2H, m); 2.59 (2H, s); 3.09 (1H, t, $J = 8.0$ Hz); 7.35–7.52 (2H, m); 7.65–7.78 (2H, m).

Compound **3d**, **4d** and **6d**: see above.

Electrolysis of 2e in the presence of isopropyl bromide. Compound **8e** ($R' = Pr^i$): liquid. MS: exact mass measurement: obsd, 254.1343; calcd for $C_{14}H_{22}O_2S$, 254.1340. 300 MHz ^{1}H NMR δ: 0.86 (3H, t, $J = 6.8$ Hz); 1.17–1.46 (4H, m); 1.29 (6H, d, $J = 7.0$ Hz); 1.66–1.79 (2H, m); 3.01 (1H, hept, $J = 6.9$ Hz); 3.07 (2H, t, $J = 8.1$ Hz); 7.48 (1H, dd, $^3J = 7.7$ and 7.7 Hz); 7.52 (1H, ddd, $^3J = 7.7$ Hz, $^4J = 1.9$ and 1.9); 7.72 (1H, ddd, $^3J = 7.7$, $^4J = 1.9$ and 1.9 Hz), 7.76 (1H, dd, $^4J = 1.9$ and 1.9 Hz). 75 MHz ^{13}C NMR δ: 13.69; 22.11; 22.25; 23.77 (2C); 30.341; 34,12; 56.30; 125.50; 125.87; 129.27; 131.89; 139.15; 150.46.

Compound **9e** ($R' = Pr^i$): liquid. MS: exact mass measurement: obsd, 254.1343; calcd for $C_{14}H_{22}O_2S$, 254.1340. 300 MHz ^{1}H NMR δ: 0.86 (3H, t, $J = 7.0$ Hz); 1.15–1.43 (4H, m); 1.32 (6H, d, $J = 6.8$ Hz); 1.56–1.82 (2H, m); 3.13 (2H, t, $J = 8.0$ Hz); 3.89 (1H, hept, $J = 6.8$ Hz); 7.35 (1H, ddd, $^3J = 7.6$ and 8.0 Hz, $^4J = 1.3$ Hz); 7.51 (1H, dd, $^3J = 7.9$ Hz, $^4J = 1.3$ Hz); 7.58 (1H, ddd, $^3J = 7.6$ and 7.9 Hz, $^4J = 1.3$ Hz), 8.0 (1H, dd, $^3J = 8.0$ Hz, $^4J = 1.3$ Hz).

Compound **10e** ($R' = Pr^i$): liquid. 300 MHz ^{1}H NMR δ: 0.86 (6H, t, $J = 7.0$ Hz); 1.15–1.43 (8H, m); 1.33 (6H, d, $J = 6.9$ Hz); 1.56–1.82 (12H, m); 3.09 (1H, hept, $J = 6.8$ Hz); 3.61 (2H, t, $J = 8.0$ Hz); 3.64 (2H, t, $J = 8.0$ Hz); 7.60 (1H, dd, $^3J = 8.0$ Hz, $^4J = 1.8$ Hz); 8.08 (1H, d, $^4J = 1.6$ Hz); 8.18 (1H, d, $^3J = 8.0$ Hz)

Compound **6e**: see above.

Electrolysis of 2f in the presence of isobutyl bromide. Compound **8f** ($R' = Bu^i$): liquid. MS: exact mass measurement: obsd, 282.1640; calcd for $C_{16}H_{26}O_2S$, 282.1653. 300 MHz ^{1}H NMR δ: 0.82 (3H, t, $J = 7.4$ Hz); 0.85 (3H, t, $J = 7.7$ Hz); 1.16–1.49 (6H, m); 1.53–1.78 (4H, m); 1.279 (3H, d, $J = 6.9$ Hz); 2.71 (1H, tq, $J = 6.9$ and 7.1 Hz); 3.08 (2H, t, $J = 8.0$ Hz); 7.43–7.55 (2H, m); 7.67–7.76 (2H, m). 75 MHz ^{13}C NMR δ: 13.88; 13.95; 21.58; 22.25; 22.60; 27.93; 31.01; 31.16; 41.64; 56.38; 125.54; 126.54; 129.21; 132.43; 139.20; 149.35.

Compound **9f** ($R' = Bu^i$): liquid. MS: exact mass measurement: obsd, 282.1640; calcd for $C_{16}H_{26}O_2S$, 282.1653. 300 MHz ^{1}H NMR δ: 0.85 (3H, t, $J = 6.8$ Hz); 0.87 (3H, t, $J = 7.3$ Hz); 1.17–1.46 (4H, m); 1.54–1.78 (6H, m); 1.29 (3H, d, $J = 6.8$ Hz); 3.13 (2H, t, $J = 8.1$ Hz); 3.64 (1H, tq, $J = 6.8$ and 7.1 Hz); 7.35 (1H, ddd, $^3J = 7.5$ and 8.0 Hz, $^4J = 1.2$ Hz); 7.46 (1H, dd, $^3J = 7.9$ Hz, $^4J = 1.2$); 7.59 (1H, ddd, $^3J = 7.5$ and 7.9 Hz, $^4J = 1.2$ Hz), 8.01 (1H, dd, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz). 75 MHz ^{13}C NMR δ: 12.29; 13.89; 22.28; 22.57 (2C); 28.02; 31.12; 31.17; 36.11; 56.82; 126.20; 128.04; 130.19; 133.80; 137.05; 148.42.

Electrolysis of 2e in the presence of (*R*)-2-bromooctane. Compound **8e** [$R' = CH(CH_3)(C_6H_{13})$], racemic: liquid. 300 MHz ^{1}H NMR δ: 0.86 (6H, t, $J = 7.1$ Hz); 1.26 (3H, t, $J = 6.9$ Hz); 1.15–1.43 (12H, m); 1.53–1.64 (2H, m); 1.65–1.78 (2H, m); 2.77 (1H, tq, $J = 6.9$ and 7.1 Hz); 3.07 (2H, t, $J = 8.1$ Hz); 7.43–7.50 (2H, m); 7.68–7.76 (2H, m). 75 MHz ^{13}C NMR δ: 13.67; 14.06; 22.07; 22.11; 22.36; 22.61; 27.57; 29.27; 30.37; 31.75; 38.22; 39.96; 56.36; 125.51; 126.49; 129.23; 132.38; 139.14; 149.67.

Compound **9e** [$R' = CH(CH_3)(C_6H_{13})$], racemic: liquid. 300 MHz ^{1}H NMR δ: 0.86 (9H, t, $J = 6.89$ Hz); 1.29 (3H, t, $J = 7.0$ Hz); 1.14–1.45 (14H, m); 1.53–1.79 (8H, m); 2.89 (1H, tq, $J = 7.1$ and 7.1 Hz); 3.62 (4H, t, $J = 7.8$ Hz); 7.61 (1H, dd, $^3J = 8.1$ Hz, $^4J = 1.8$ Hz); 8.08 (1H, d, $^4J = 1.8$ Hz); 8.20 (1H, d, $^3J = 8.1$ Hz).

Compound **3e**: see above.

Compound **10e** [$R' = CH(CH_3)(C_6H_{13})$]; racemic: liquid. 300 MHz ^{1}H NMR δ: 0.86 (6H, t, $J = 6.8$ Hz); 1.27 (3H, t, $J = 7.0$ Hz); 1.15–1.45 (12H, m); 1.53–1.79 (4H, m); 3.13 (2H, t, $J = 8.1$ Hz); 3.69 (1H, tq, $J = 6.8$ and 6.8 Hz); 7.35 (1H, ddd, $^3J = 8.0$ and 8.0 Hz, $^4J = 1.1$ Hz); 7.47 (1H, dd, $^3J = 7.8$, $^4J = 1.1$ Hz); 7.59 (1H, ddd, $^3J = 7.8$ and 8.0 Hz, $^4J = 1.3$ Hz), 8.00 (1H, dd, $^3J = 8.0$ Hz, $^4J = 1.3$ Hz).

Electrolysis of 2b in the presence of 1,4-dibromobutane. Compound **8b** [$R' = (CH_2)_4Br$]: liquid. MS: exact mass measurement: obsd, 304.0141; calcd for $C_{12}H_{17}O_2SBr$, 304.0132. 300 MHz ^{1}H NMR δ: 1.28 (3H, t, $J = 7.4$ Hz); 1.76–1.97 (4H, m); 2.74 (2H, t, $J = 7.4$ Hz); 3.12 (2H, q, $J = 7.4$ Hz); 3.43 (2H, t, $J = 6.4$ Hz); 7.44–7.54 (2H, m); 7.70–7.78 (2H, m). 75 MHz ^{13}C NMR δ: 7.49; 29.56; 32.11; 33.30; 34.79; 50.65; 125.90; 127.88; 129.39; 133.80; 138.70; 143.53.

Compound **9b** [$R' = (CH_2)_4Br$]: liquid. MS: exact mass measurement: obsd, 304.0140; calcd for $C_{12}H_{17}O_2SBr$, 304.0132. 300 MHz ^{1}H NMR δ: 1.27 (3H, t, $J = 7.4$ Hz); 1.78–1.93 (2H, m); 1.92–2.06 (2H, m); 3.05 (2H, t, $J = 7.8$ Hz); 3.15 (2H, q, $J = 7.4$ Hz); 3.46 (2H, t, $J = 6.6$ Hz); 7.39 (1H, ddd, $^3J = 7.5$ and 8.3 Hz, $^4J = 1.3$ Hz); 7.40 (1H, dd, $^3J = 7.5$ Hz, $^4J = 1.3$ Hz); 7.57 (1H, ddd, $^3J = 7.5$ and 7.5 Hz, $^4J = 1.4$ Hz), 7.99 (1H, dd, $^3J = 8.3$ Hz, $^4J = 1.4$ Hz).

Compound **6b**: see above.

Electrolysis of 2c in the presence of 1,4-dibromobutane. Compound **8c** [$R' = (CH_2)_4Br$]: liquid. MS: exact mass measurement: obsd, 318.0291; calcd for $C_{13}H_{19}O_2SBr$, 318.0289. 300 MHz ^{1}H NMR δ: 1.00 (3H, t, $J = 7.4$ Hz); 1.68–1.96 (6H, m); 2.74 (2H, t, $J = 7.4$ Hz); 3.07 (2H, t, $J = 8.0$ Hz); 3.43 (2H, t, $J = 6.4$ Hz); 7.44–7.53 (2H, m); 7.70–7.78 (2H, m). 75 MHz ^{13}C NMR δ: 13.10; 16.52; 29.52; 32.08; 33.22; 34.76; 58.05; 125.73; 127.71; 129.34; 133.67; 138.36; 143.48.

Compound **9c** [$R' = (CH_2)_4Br$]: liquid. 300 MHz ^{1}H NMR δ: 1.00 (3H, t, $J = 7.5$ Hz); 1.66–1.81 (2H, m); 1.78–1.93 (2H, m); 1.92–2.06 (2H, m); 3.04 (2H, t, $J = 7.9$ Hz); 3.10 (2H, t, $J = 8.0$ Hz); 3.46 (2H, t, $J = 6.5$ Hz); 7.38 (1H, ddd, $^3J = 7.5$ and 7.7 Hz, $^4J = 1.3$ Hz); 7.40 (1H, dd, $^3J = 7.5$ Hz, $^4J = 1.3$ Hz); 7.57 (1H, ddd, $^3J = 7.5$ and 7.5 Hz, $^4J = 1.4$ Hz), 8.00 (1H, dd, $^3J = 7.7$ Hz, $^4J = 1.4$ Hz). 75 MHz ^{13}C NMR δ: 13.04; 16.43; 30.68; 32.18; 32.53; 33.49; 58.36; 126.80; 130.60; 131.71; 133.70; 137.16; 142.26.

Electrolysis of 2b in the presence of 1,6-dibromohexane. Compound **8b** [$R' = (CH_2)_6Br$]: liquid. MS: exact mass measurement: obsd, 332.0450; calcd for $C_{14}H_{21}O_2SBr$, 332.0445. 300 MHz ^{1}H NMR δ: 1.28 (3H, t, $J = 7.5$ Hz); 1.36–1.58 (4H, m); 1.59–1.79 (2H, m); 1.80–1.94 (2H, m); 2.70 (2H, t, $J = 7.6$ Hz); 3.11 (2H, t, $J = 7.5$ Hz); 3.40 (2H, t, $J = 6.7$ Hz); 7.44–7.51 (2H, m); 7.68–7.76 (2H, m).

Compound **9b** [R′ = $(CH_2)_6Br$]: liquid. MS: exact mass measurement: obsd, 332.0450; calcd for $C_{14}H_{21}O_2SBr$, 332.0445. 300 MHz ^1H NMR δ: 1.24 (3H, t, J = 7.5 Hz); 1.35–1.58 (4H, m); 1.59–1.79 (2H, m); 1.80–2.94 (2H, m); 3.00 (2H, t, J = 8.0 Hz); 3.14 (2H, t, J = 7.5 Hz); 3.41 (2H, t, J = 6.8 Hz); 7.36 (1H, ddd, ^3J = 7.5 and 8.2 Hz, ^4J = 1.3 Hz); 7.38 (1H, dd, ^3J = 7.4 Hz, ^4J = 1.3 Hz); 7.55 (1H, ddd, ^3J = 7.4 and 7.5 Hz, ^4J = 1.4 Hz), 7.99 (1H, dd, ^3J = 8.2 Hz, ^4J = 1.4 Hz).

Compound **3b**, **4b** and **6b**: see above.

Electrolysis of 2c in the presence of 1,10-dibromodecane. Compound **8c** [R′ = $(CH_2)_{10}Br$]: liquid. MS: exact mass measurement: obsd, 402.1206; calcd for $C_{19}H_{31}O_2SBr$, 402.1228. 200 MHz ^1H NMR δ: 1.00 (3H, t, J = 7.4 Hz); 1.17–1.51 (12H, m); 1.54–1.93 (6H, m); 2.70 (2H, t, J = 7.7 Hz); 3.07 (2H, t, J = 8.0 Hz); 3.41 (2H, t, J = 6.8 Hz); 7.43–7.52 (2H, m); 7.66–7.76 (2H, m). 75 MHz ^{13}C NMR δ: 12.97; 16.51; 28.12; 28.71; 29.14; 29.34; 29.37 (2C); 31.16; 32.80; 34.09; 35.66; 57.98; 125.34; 127.69; 129.15; 133.75; 139.02; 144.49.

Compound **9c** [R′ = $(CH_2)_{10}Br$]: liquid. MS: exact mass measurement: obsd, 402.1206; calcd for $C_{19}H_{31}O_2SBr$, 402.1228. 200 MHz ^1H NMR δ: 0.99 (3H, t, J = 6.8 Hz); 1.13–1.52 (12H, m); 1.52–1.96 (6H, m); 3.00 (2H, t, J = 7.9 Hz); 3.10 (2H, t, J = 8.0 Hz); 3.41 (2H, t, J = 6.8 Hz); 7.36 (1H, ddd, ^3J = 7.5 and 7.5 Hz, ^4J = 1.3 Hz); 7.38 (1H, dd, ^3J = 7.5 Hz, ^4J = 1.3 Hz); 7.55 (1H, ddd, ^3J = 7.5 and 8.1 Hz, ^4J = 1.3 Hz), 7.99 (1H, dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz). 75 MHz ^{13}C NMR δ: 13.02; 16.41; 28.14; 28.73; 29.41 (3C); 29.73; 32.25; 32.76; 33.09; 34.10; 58.13; 126.36; 130.39; 131.62; 133.49; 136.89; 143.18.

Electrolysis of 2d in the presence of (±)-1-bromo-3-chloro-2-methylpropane. Compound **8d** [R′ = $CH_2CH(CH_3)(CH_2Cl)$]: liquid. MS: exact mass measurement: 288.0949; calcd for $C_{14}H_{21}O_2SCl$, 288.0951. 300 MHz ^1H NMR δ: 0.89 (3H, t, J = 7.3 Hz); 1.03 (3H, d, J = 6.7 Hz); 1.39 (2H, m); 1.69 (2H, m); 2.18 (1H, m); 2.77 (2H, AB_X, J_{AB} = 13.6 Hz); 3.09 (2H, t, J = 8.0 Hz); 3.43 (2H, AB_X, J_{AB} = 10.8 Hz); 7.45–7.54 (2H, m); 7.72–7.79 (2H, m). 75 MHz ^{13}C NMR δ: 13.48; 17.56; 21.56; 24.71; 37.29; 39.80; 49.90; 56.16; 125.99; 128.50; 129.39; 134.44; 139.58; 141.65.

Compound **9d** [R′ = $CH_2CH(CH_3)(CH_2Cl)$]: liquid. MS: exact mass measurement: obsd, 288.0951; calcd for $C_{14}H_{21}O_2SCl$, 288.0951. 300 MHz ^1H NMR δ: 0.89 (3H, t, J = 7.3 Hz); 1.07 (3H, d, J = 6.7 Hz); 1.39 (2H, m); 1.57–1.75 (2H, m); 2.39 (1H, m); 3.03 (2H, AB_X, J_{AB} = 13.4 Hz); 3.10 (2H, t, J = 8.1 Hz); 3.54 (2H, AB_X, J_{AB} = 4.6 Hz); 7.40 (1H, dd, ^3J = 7.4, ^4J = 1.4 Hz); 7.45 (1H, ddd, ^3J = 7.5 and 7.9 Hz, ^4J = 1.4 Hz); 7.57 (1H, ddd, ^3J = 7.4 and 7.5 Hz, ^4J = 1.5 Hz), 8.02 (1H, dd, ^3J = 7.9 Hz, ^4J = 1.5 Hz). 75 MHz ^{13}C NMR δ: 13.52; 17.61; 21.57; 24.57; 37.08; 37.36; 50.66; 56.56; 127.15; 130.93; 132.36; 133.44; 137.75; 140.39.

Electrolysis of 2b in the presence of 6-bromohex-1-ene. Compound **8b** [R′ = $(CH_2)_4CH{=}CH_2$]: liquid. 300 MHz ^1H NMR δ: 1.29 (3H, t, J = 7.4 Hz); 1.37–1.77 (4H, m); 2.08 (2H, dt, J = 6.7 and 6.7 Hz); 2.71 (2H, m, J = 7.6 Hz); 3.11 (2H, q, J = 7.4 Hz); 4.94 (1H, ddt, $^2J_{gem}$ = 2.1 Hz, $^3J_{cis}$ = 10.3, $^4J_{cis}$ = 1.1 Hz); 5.00 (1H, ddt, $^2J_{gem}$ = 2.1 Hz, $^3J_{trans}$ = 17.06 Hz, $^4J_{trans}$ = 1.6 Hz); 5.79 (1H, ddt, ^3J = 6.7 Hz, $^3J_{cis}$ = 10.3 Hz and $^3J_{trans}$ = 17.1 Hz); 7.42–7.49 (2H, m); 7.67–7.76 (2H, m). 75 MHz ^{13}C NMR δ: 6.59; 24.94; 28.43; 30.59; 33.50; 50.66; 77.36; 114.74; 125.66; 127.89; 129.20; 133.79; 138.46; 144.36.

Compound **9b** [R′ = $(CH_2)_4CH{=}CH_2$]: liquid. 300 MHz ^1H NMR δ: 1.26 (3H, t, J = 7.5 Hz); 1.45–1.81 (4H, m); 2.11 (2H, dt, J = 6.7 and 7.3 Hz); 3.01 (2H, t J = 7.8 Hz); 3.15 (2H, q, J = 7.5 Hz); 4.95 (1H, ddt, $^2J_{gem}$ = 2.1 Hz, $^3J_{cis}$ = 10.2, $^4J_{cis}$ = 1.1 Hz); 5.02 (1H, ddt, $^2J_{gem}$ = 2.1 Hz, $^3J_{trans}$ = 17.06 Hz, $^4J_{trans}$ = 1.8 Hz); 5.82 (1H, ddt, ^3J = 6.7 Hz, $^3J_{cis}$ = 10.2 Hz and $^3J_{trans}$ = 17.1 Hz); 7.38 (1H, dd, ^3J = 7.5, ^4J = 1.3 Hz); 7.37 (1H, ddd, ^3J = 7.5 and 8.3 Hz, ^4J = 1.3 Hz); 7.55 (1H, ddd, ^3J = 7.5 and 7.5 Hz, ^4J = 1.3 Hz), 7.98 (1H, dd, ^3J = 8.3 Hz, ^4J = 1.3 Hz). 75 MHz ^{13}C NMR δ: 7.27; 24.85; 28.90; 31.64; 33.50; 50.73; 77.23; 114.61; 126.42; 130.66; 131.67; 133.56; 138.65; 143.13.

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