Cathodic Behaviour of 1-Cycloalken-1-yl Phenyl Sulfones. I. Competition among Dimerization, Cleavage, Isomerization and Oligomerization Processes in Aprotic Media

Sylvie Prigent,[a] Pascal Cauliez,*,[a] Jacques Simonet[a] and Dennis G. Peters*,[b]

[a]Laboratoire d'Electrochimie associé au CNRS, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes, France and [b]Department of Chemistry, Indiana University, Bloomington, Indiana 47405, USA

Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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1-Cycloalken-1-yl phenyl sulfones **1a** and **1b** have been studied electrochemically in aprotic media (N,N-dimethylformamide, dimethyl sulfoxide, or acetonitrile containing tetraalkylammonium salts) at a mercury electrode. Their behaviour has been compared with that of 2-norbornen-2-yl phenyl sulfone **1c**. The expected cleavage reaction is accompanied by a concomitant isomerization process into allyl sulfones that is triggered by electrogenerated bases. A quantitative determination of the product distribution during controlled-potential electrolyses suggests the formation of dimers and oligomeric species, arising through a Michael addition of the sulfone anions to the activated double bond of these sulfones.

Arylsulfonyl groups are more and more commonly used in organic synthesis as either protecting or activating groups.[1] For example, as electron-withdrawing groups, they can activate double or triple bonds towards nucleophilic conjugate-addition reactions without presenting the drawbacks of carbonyl groups (competition with 1,2-addition or enolization).[2] Moreover, alkyn-1-yl aryl sulfones ($RC \equiv SO_2Ar$) are good dienophiles for Diels–Alder reactions and dipolarophiles for 1,3-dipolar cycloadditions affording vinyl sulfones.[3] However, since the sulfonyl group is almost never required in the target molecule, specific reactions to remove the activating arylsulfonyl groups from vinyl sulfones are needed. Electrochemical reduction is a good candidate for achieving this goal. In this context, we have been interested in the systematic study of the cathodic behaviour of vinyl sulfones.[4,5] So far, mostly acyclic compounds have been investigated, and 1-cycloalken-1-yl phenyl sulfones **1a** and **1b** have not yet been studied electrochemically.

2-Norbornen-2-yl phenyl sulfone (**1c**) was chosen for comparison purposes, because of its inability to undergo an allylic isomerization process and also because its
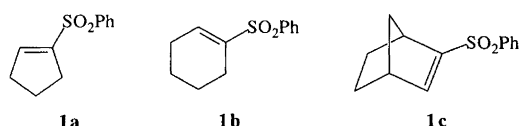
Scheme 1.

greater ring strain should influence its electrochemical behaviour.

In order to have a better understanding of the electrochemical processes involved, a quantitative determination of the product distributions has been undertaken. We have achieved this by performing controlled-potential electrolyses in a sealed electrochemical cell and by detecting and quantitating the products with the help of gas chromatography–mass spectrometry (GC–MS).

Experimental

Synthesis of sulfones **1** *and* **2**. Sulfones **1a–c** were prepared in good yields from the corresponding cycloalkenes and thiophenol as already described:[6] phenylsulfenyl chloride (from thiophenol and N-chlorosuccinimide) was reacted with the cyclic olefins and the resulting *trans*-β-chlorophenyl sulfides were oxidized to the corresponding

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* To whom correspondence should be addressed.

trans-β-chlorophenyl sulfones, which may then be dehydrochlorinated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under mild conditions. Spectral data not previously available are reported below.

2-Cyclopenten-1-yl phenyl sulfone **2a** was obtained by chemical isomerization of the corresponding vinyl sulfone **1a** under basic conditions (tetrabutylammonium hydroxide in DMF) in a similar way as previously described with other bases.[7]

Spectral data of substrates. ^{13}C NMR spectra were recorded on a Bruker AC300P apparatus at 300 MHz. GC–MS electron-impact data were acquired at 70 eV with a Hewlett-Packard 5890 Series II gas chromatograph coupled to a Hewlett-Packard model 5971 mass-selective detector.

1-Cyclopenten-1-yl phenyl sulfone (**1a**): ^{13}C NMR (75 MHz, CDCl$_3$): δ 23.6 (tm, J = 133 Hz, CH$_2$), 30.8 (tm, J = 130 Hz, CH$_2$), 32.9 (tm, J = 130 Hz, CH$_2$), 127.8 (ddd, J = 164.6, 7.6 and 7.4 Hz, 2 CH$_{arom.meta}$), 129.1 (dd, J = 163.8 and 7.6 Hz, 2 CH$_{arom.ortho}$), 133.3 (dt, J = 161.7 and 7.4 Hz, CH$_{arom.para}$), 139.5 (t, J = 8.3 Hz, C$_{arom.}$), 143.4 (dm, J = 164.8 Hz, CH$_{vinyl}$), 144.5 (m, C$_{vinyl}$). MS, m/z (relative intensity): 125 (100), 83 (59), 55 (42), 67 (38), 77 (33), 41 (32), 51 (31), 126 (30), 39 (29), 66 (26), 65 (21), 208 (M^+, 20).

1-Cyclohexen-1-yl phenyl sulfone (**1b**): ^{13}C NMR (75 MHz, CDCl$_3$): δ 20.8 (tm, J = 129 Hz, CH$_2$), 21.8 (tm, J = 130 Hz, CH$_2$), 22.8 (tm, J = 131 Hz, CH$_2$), 25.5 (tm, J = 127 Hz, CH$_2$), 128.0 (ddd, J = 164.5, 6.9 and 6.9 Hz, 2 CH$_{arom.meta}$), 129.1 (dd, J = 163 and 7.5 Hz, 2 CH$_{arom.ortho}$), 133.15 (dt, J = 163 and 7.2 Hz, CH$_{arom.para}$), 138.5 (dm, J = 163 Hz, CH$_{vinyl}$), 139.4 (t, J = 7.9 Hz, C$_{arom.}$), 139.75 (m, C$_{vinyl}$). MS, m/z (relative intensity): 222 (M^+, 100), 79 (66), 81 (63), 77 (33), 97 (32), 125 (32), 51 (26), 53 (24), 69 (23).

2-Norbornen-2-yl phenyl sulfone (**1c**): ^{13}C NMR (75 MHz, CDCl$_3$): δ 24.7 (tm, J = 137 Hz, CH$_2$), 24.8 (tm, J = 137 Hz, CH$_2$), 43.0 (dm, J = 150 Hz, CH), 43.6 (dm, J = 150 Hz, CH), 49.3 (tm, J = 137 Hz, CH$_2$), 127.7 (ddd, J = 164, 7.3 and 7.7 Hz, 2 CH$_{arom.meta}$), 129.2 (dd, J = 163.3 and 7.3 Hz, 2 CH$_{arom.ortho}$), 133.3 (dt, J = 161.9 and 8.0 Hz, CH$_{arom.para}$), 140.3 (t, J = 8.0 Hz, C$_{arom.}$), 146.1 (dm, J = 175 Hz, CH$_{vinyl}$), 147.9 (m, C$_{vinyl}$). MS, m/z (relative intensity): 81 (100), 77 (62), 125 (51), 206 (36), 79 (35), 126 (27), 51 (25), 39 (25), 53 (24) 234 (M^+, 6).

Solvents and electrolytes. *N,N*-Dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and acetonitrile were Burdick and Jackson 'distilled in glass' reagents and were used as received. The supporting electrolytes were tetramethylammonium tetrafluoroborate (TMABF$_4$), tetraethylammonium perchlorate (TEAP), tetrabutylammonium tetrafluoroborate (TBABF$_4$), and tetrabutylammonium perchlorate (TBAP). They were obtained from GFS Chemicals Inc., stored in a vacuum

oven at 65 °C, and used without further purification. All deaeration procedures were accomplished with Air Products UHP-grade argon.

Cells, electrodes and instrumentation. Earlier publications[8] give detailed information about the cells and instrumentation for both cyclic voltammetry and controlled-potential electrolysis. All potentials are quoted with respect to a reference electrode consisting of a cadmium-saturated mercury amalgam in contact with DMF saturated with both cadmium chloride and sodium chloride; this electrode has a potential of −0.76 V vs. the aqueous saturated calomel electrode (SCE) at 25 °C.[9]

High scan rate cyclic voltammetry was performed with an Autolab PGSTAT20 from Eco Chemie, equipped with General Purpose Electrochemical System software (version 4.4 for Windows), or with an EG&G PAR model 175 coupled to a model 310 Nicolet oscilloscope, in a three-electrode cell, and with a hanging mercury drop as the working electrode.

Current–time curves for chronoamperometry and controlled-potential electrolysis were acquired, stored, and processed by means of locally written software, which controlled a Tecmar data acquisition board in an IBM personal computer.

Identification and quantitation of electrolysis products. Electrolysis products were identified with the aid of gas chromatography–mass spectrometry (GC–MS) either by comparison of their chromatographic retention times with those of commercially available (for **3a–c**, **7**) or synthesized (**1a–c**, **2a**) authentic compounds, by comparison of their mass spectra with those described in the literature (for **4b**,[10] **5a**,[11] **5b**,[12] **6a**[13] and **8**[14]), or by analysis of their mass spectral data [**2b** m/z (relative intensity) 81 (100), 79 (23), 77 (13), 143 (11), 85 (9.5), 53 (8), 82 (7); **4a** m/z (relative intensity) 91 (100), 92 (45), 134 (M^+, 35), 93 (33) 66 (32), 106 (26), 77 (26) 119 (13); **9b** m/z (relative intensity) 83 (100), 55 (55), 41 (26), 39 (12), 80 (11), 81 (9), 122 (M^+, 1.2); **10c** m/z (relative intensity) 67 (100), 95 (79), 80 (63), 66 (50), 79 (43), 41 (38), 81 (35), 123 (32), 190 (M^+, 16)]. The products were quantitated by means of gas chromatography, as previously described.[15] A 30 m × 0.53 mm capillary column (AT-35, Alltech Associates) with a stationary phase of poly(phenylmethylsiloxane) was employed. A known quantity of an electroinactive internal standard (*n*-nonane or *n*-tetradecane) was added to each solution before the start of the electrolysis. Methyl iodide (fivefold excess) was added to the electrolysed solution and the reaction mixture was stirred at room temperature for 1 h in order to trap the sulfinate anions as methyl phenyl sulfone (**7**) or methyl phenylsulfinate (**8**). All yields reported represent the absolute percentage of starting material incorporated into a particular species.

Results

Cyclic voltammetry. In an aprotic solvent (DMF, DMSO or acetonitrile) containing a tetrabutylammonium salt (TBABF$_4$ or TBAP), sulfones **1a–c** all exhibit, at a hanging mercury drop electrode at moderate scan rates, a single irreversible cathodic wave (peak A) within the explored cathodic range [up to -2.0 V vs. Cd(Hg) electrode] (Fig. 1). At larger sweep rates, this step becomes totally reversible, allowing the determination of the formal standard potentials $E^{\circ\prime}$ (see Table 1).

With sulfones **1a** and **1b**, a prepeak (peak B) appears and grows with repetitive sweeps. Moreover, small oxidation peaks (peaks C and D) that could be attributed to the oxidation of carbanionic species were observed. The intensity of these three peaks increases upon recurrent scans, contrary to what is observed (as expected) for the main peak. When activated neutral alumina was added to the electrolytic medium, the size of the three additional peaks dropped whereas that of the main peak increased. On the other hand, addition of varying amounts of base (tetrabutylammonium hydroxide, potassium *tert*-butoxide or DBU) showed the opposite effect.

Similarly, in aprotic DMF containing TEAP, the allylic sulfone **2a** exhibits, under the same experimental conditions at moderate scan rates, a fully irreversible cathodic

step [peak B, $E_p = -1.39$ V vs. Cd(Hg)] as well as small oxidation peaks C and D in the same potential range as obtained with **1a**. However, the cathodic step remains totally irreversible at higher sweep rates (up to 1000 V s^{-1}) which suggests that the rate constant (k_c) for cleavage of the C–S bond is more than ca. 5×10^4 s^{-1}.

2a   **2b**
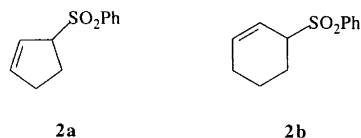
Scheme 2.

Macroelectrolyses. Exhaustive electrolyses were carried out at a potential close to that of peak A. Current–time curves show peculiar behaviour in the case of **1a** and **1b** (a pronounced maximum is observed, Fig. 2) whereas the current–time curve for **1c** exhibits a normal decrease with time. Such a phenomenon might be attributed to the formation *in situ* of species more electroactive than the starting sulfone. It should be noted that the current maximum appears earlier with sulfone **1a** than with sulfone **1b** (e.g., 1 vs. 6 min, respectively). Moreover, the
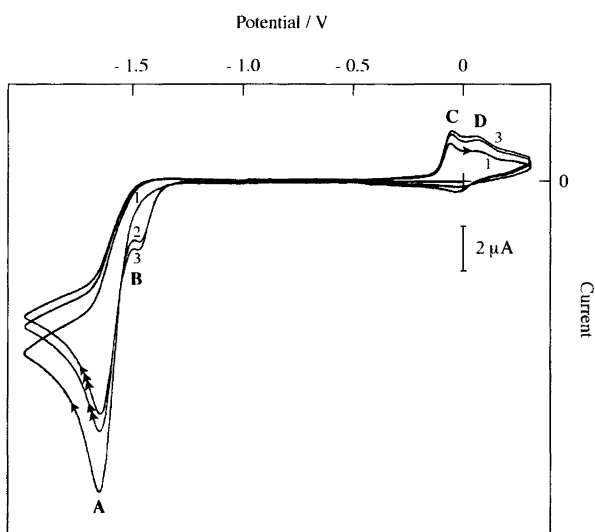

Fig. 1. Cyclic voltammetry (first three sweeps) of sulfone **1b** (10 mM) in DMF–0.1 M TBAP at a hanging mercury drop electrode (area 1.4 mm^2), $v = 500$ mV s^{-1}.

Table 1. Peak potentials at 100 mV s^{-1} and formal standard potentials for sulfones **1a–c** in DMF containing 0.1 M tetra-alkylammonium salts. Hanging mercury drop electrode (area 1.4 mm^2). Reference system: Cd(Hg)/CdCl$_2$/Cl$^-_{\text{satd.}}$.

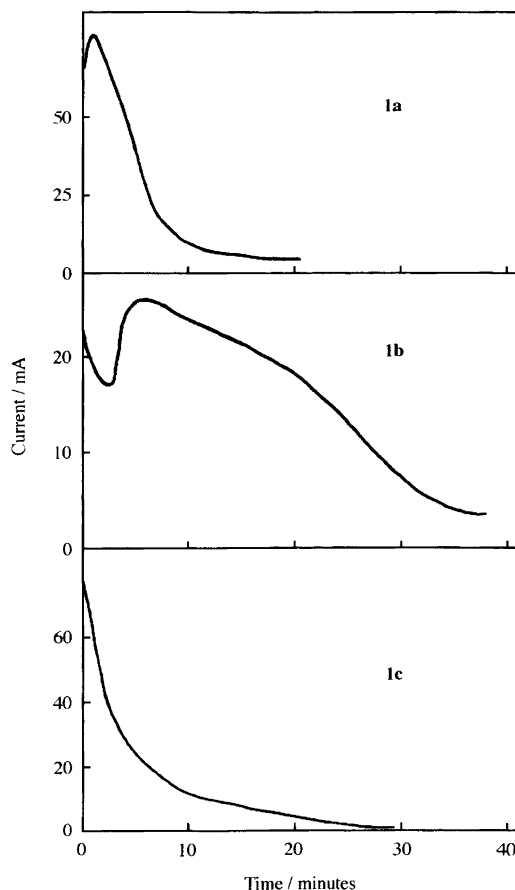| Substrate	Supporting electrolyte	C/mM	E_{pA}/V	E_{pB}/V	E'°/V
1a	TBABF$_4$	2.2	-1.46	-1.35	-1.45
1b	TBAP	5.0	-1.57	-1.37	-1.53
1c	TMABF$_4$	1.5	-1.46	—	-1.43

Fig. 2. Current–time curves for the controlled-potential reduction of 10 mM **1a–c** in DMF–0.1 M TEAP (for **1a**) or TBABF$_4$ (for **1b** and **1c**) at -1.46 V (for **1a**), -1.60 V (for **1b** and **1c**) at a mercury pool cathode (area 9 cm^2).

current increase is accompanied by the appearance of a deep orange colour in the reaction medium that persists until the end of the electrolysis.

Coulometric data and product distributions for electrolytic reduction of 1-cyclopenten-1-yl phenyl sulfone 1a (10 mM) at a mercury pool cathode in DMF containing 0.1 M TEAP are gathered in Table 2. Each entry is the average of at least three separate experiments, and the reproducibilities of the n values and product yields are ±0.05 and ±5%, respectively. The analytical technique used allowed only the detection of low molecular weight products, which may account for the low total yields obtained in these experiments.

3a   **4a**   **5a**   **6a**
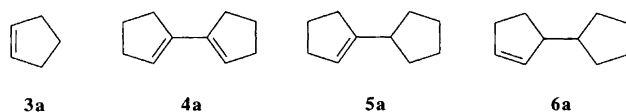
Scheme 3.

After consumption of approximately 0.5 electron per molecule of substrate, most of the starting sulfone 1a had reacted and the allylic isomer 2-cyclopenten-1-yl phenyl sulfone (2a) was then the main compound detected remaining as acceptor in the catholyte. When the electrolysis current had decayed to the background level, the coulometric n value was approximately 1.7 and an analysis of the solution for products revealed the presence of cyclopentene (3a, 49%) as the main product, as well as dimeric products 4a (2%), 5a (4%), and 6a (3%), which are seen only at the end of the electrolysis. With lower sulfone concentrations (5 mM), the dimeric compounds were not detected. The global yield based on the cyclopentenyl moiety (total 1) was low (58%) whereas that based on the phenyl moiety [total 2, obtained by addition of methyl iodide at the end of the electrolysis

to trap the phenyl sulfinate anions as methyl phenyl sulfone (7) or methyl phenylsulfinate (8)] was somewhat larger (85%) although still not quantitative. When the electrolysis solution was stirred without applied potential for 30 min after preliminary consumption of 0.1 electron per sulfone molecule, the amount of allylic sulfone 2a increased whereas that of vinylic sulfone 1a decayed. Similar results were obtained when the electrolyses were performed with glassy carbon electrodes.

In another experiment (Table 3), after the electrolysis current had decayed to the background level, the potential was stepped to a more negative value (−2.0 V) and the electrolysis resumed until the current decayed once again to the background level. The coulometric n value then increased to 1.92 and the global yield (total 2) became nearly quantitative (96%).

Cyclic voltammograms recorded during and at the end of the electrolysis (without opening of the cell) confirmed the rapid disappearance of sulfone 1a as well as the formation of its isomer 2a characterized by a less negative peak potential (−1.39 V).

Coulometric data and product distributions for electrolytic reduction of 1-cyclohexen-1-yl phenyl sulfone 1b (10 mM) at a mercury pool cathode in DMF containing 0.1 M TEAP are compiled in Table 4.

When one compares the results from these electrolysis procedures with those regularly obtained from 1a, one sees a similar product distribution, except that the yield of cyclohexene is much larger (90%). Thus, the isomerization process, leading to the formation of allylic sulfone 2b concomitantly with the disappearance of vinyl sulfone 1b at the beginning of the electrolysis, is slower for 1-cyclohexen-1-yl phenyl sulfone (1b). The addition of norbornene (3c) in large excess as radical scavenger in the preparative-scale electrolyses of 1a and 1b does not significantly change the product distribution.

Other solvents have been used for the electrolysis of 1b. DMF-d_7 does not significantly affect the product distribution nor the coulometric n values and no deuteriated products could be detected by GC–MS. When the electrolyses are performed in acetonitrile containing 0.1 M TMABF₄, a significant amount (32%) of

Table 2. Percentage distribution of species during controlled-potential reduction of 1a (10 mM) in DMF containing 0.1 M TEAP at a mercury pool cathode (area 9 cm²) at − 1.46 V vs. $Cd(Hg)/CdCl_2/Cl^-_{satd.}$ electrode.

| Species | Electron per molecule of starting material | | | | |
	0.1	0.1[a]	0.5	1.0	1.7
1a	33	5	2	0	0
2a	52	58	41	13	0
3a	2	2	21	38	49
4a	0	0	0	0	2
5a	0	0	0	0	4
6a	0	0	0	0	3
Total 1[b]	87	65	64	51	58
7					80[c]
8					5[c]
Total 2[d]					85[c]

[a]After stirring for 30 min without applied potential. [b]Global yield based on the cyclopentenyl moiety. [c]After addition of methyl iodide (5 equiv.) at the end of the electrolysis. [d]Global yield based on the phenyl moiety.

Table 3. Coulometric data and product distributions for controlled-potential electrolysis of 1a (10 mM) in DMF containing 0.1 M TEAP at a mercury pool cathode (area 9 cm²). The applied potential was − 1.46 V and then after completion was stepped to − 2.00 V.

| E/V | n | Product distribution (%) | | | | |
		3	5	6	Total 1[a]	Total 2[b]
−1.46	1.62	46	4	2	52	(85[c])
−2.00	1.92	46	5	2	53	96

[a]Global yield based on the cyclopentenyl moiety. [b]Global yield based on the phenyl moiety, after addition of methyl iodide (5 equiv.) at the end of the electrolysis. [c]From another experiment where the potential was not stepped to −2.00 V.

Table 4. Percentage distribution of species during controlled-potential reduction of **1b** (10 mM) in DMF containing 0.1 M TEAP at a mercury pool cathode (area 9 cm^2) at −1.60 V.

	Electron per molecule of starting material				
Species	0.1	0.1^a	0.6	1.1	1.7
1b	81	62	33	2	0
2b	12	36	20	8	0
3b	4	4	33	70	90
4b	0	0	0	0	3
5b	0	0	0	0	2
Total 1^b	97	102	86	80	95
7					96^c
8					3^c
Total 2^d					99^c

^{a}After stirring for 30 min without applied potential. ^{b}Global yield based on cyclohexenyl moiety. ^{c}After addition of methyl iodide (5 equiv.) at the end of the electrolysis. ^{d}Global yield based on the phenyl moiety.

cyclohexylacetonitrile (**9b**) is produced but the relative distribution of cyclohexene (**3b**), dimer **4b**, and dimer **5b** remains globally unchanged (55%, 2%, and 4%, respectively).

9b
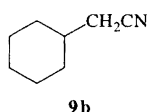
Scheme 4.

Compiled in Table 5 are results obtained from preparative-scale electrolyses of 2-norbornen-2-yl phenyl sulfone (**1c**) in DMF containing 0.1 M TEAP at −1.60 V. Norbornene (**3c**) and 2,2′-binorbornyl (**10c**) were obtained in small quantities and the global yield (total 1) is consequently low.

10c
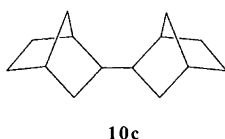
Scheme 5.

The coulometric n value is once again 1.7. A surprising feature of these experiments is the formation of norbornene at the end of the electrolysis (between coulometric n values of 0.6 and 1.7) when all the starting sulfone had already been consumed. On the other hand, the phenylsulfinate anion is obtained (after trapping with methyl iodide) in nearly quantitative yield (total 2 = 97%).

When a less negative potential was applied (−1.43 V, corresponding then to the threshold of the main cathodic peak), the coulometric n value was even lower (1.1) but the product distribution remained similar.

Table 5. Percentage distribution of species during controlled-potential reduction of **1c** (10 mM) in DMF containing 0.1 M TEAP at a mercury pool cathode (area 9 cm^2) at −1.60 V.

	Electron per molecule of starting material				
Species	0.1	0.1^a	0.6	1.1	1.7
1c	96	82	0	0	0
3c	0	0	7	14	11
10c	0	0	0	1.5	4
Total 1^b	96	82	7	15.5	15
7					92^c
8					5^c
Total 2^d					97^c

^{a}After stirring for 30 min without applied potential. ^{b}Global yield based on the norbornenyl moiety. ^{c}After addition of methyl iodide (5 equiv.) at the end of the electrolysis. ^{d}Global yield based on the phenyl moiety.

Discussion

An interpretation of the macroelectrolysis data for α-ethylenic sulfones **1a**–**c** must take into account the facts that these substrates should behave (i) as activated olefins, (ii) as substrates highly sensitive to the action of bases produced at the electrode during the course of an electrolysis, and (iii) as species for which cleavage reactions might occur in association with the electron transfer or by the action of bases – indeed the occurrence of elimination processes is well known with this kind of substrate. Obviously, the number of possible pathways could render the explanation of the distribution of reduction products unclear (or at least highly hypothetical). Nevertheless, a careful examination of the product distributions during the course of electrolysis may provide a better idea about the importance of these different pathways.

Occurrence of a dimerization reaction for sulfones **1**. Electrogenerated bases (EGBs) have been reported to convert vinyl sulfones more or less rapidly into the corresponding allyl isomers.[16] However, in the presence of lithium salts as electrophiles, the coupling of aromatic sulfones was shown[17] to proceed nicely in high yield in a stereoselective way (high excess of the ±-isomer).
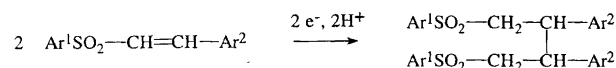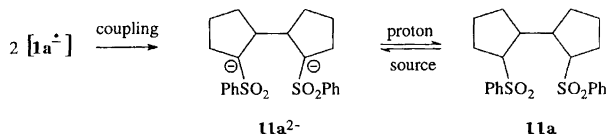

Scheme 6.

Other processes[4] not involving EGBs have also been reported for the electrocatalytic cyclodimerization of aryl vinyl sulfones, for which the cathodic reaction was found to be induced by the passage of low quantities of electricity (of the order of 0.1 F mol^{-1}). Within the range of scan rates for which the reduction processes are irreversible, sulfones **1a** and **1b** exhibit $\partial E_p/\partial \log v$ slopes close to −20 mV per decade of v (−22.6 and −19.7 mV, respectively), a result which is assignable to anion rad-
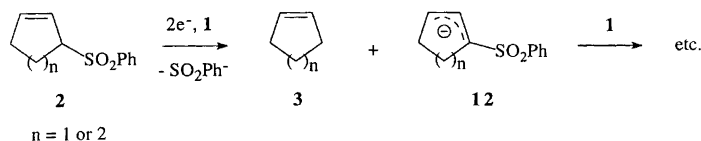
ical–anion radical coupling (in cyclic voltammetry experiments, the transformation of **1** into **2** is limited to approximately 5% between the first and second potential sweeps). Second-order kinetic constants for **1a** and **1b** were calculated according to the method described by Andrieux *et al.*[18] for a dimerization process (DIM1), and were found to be 7.6×10^4 and 1.2×10^5 s^{-1} mol^{-1} l, respectively.

Let us now consider what is going on by examining the data obtained from the macroelectrolyses, especially at the start of the cathodic reaction, when the concentration of EGBs is still small (electricity consumption of 0.1 F mol^{-1}). Thus, as shown in Table 2 for sulfone **1a**, we observe only the formation of **2a** (the allylic sulfone) together with a tiny amount of the cleavage product (cyclopentene, **3a**). Dimeric products **4a**, **5a** and **6a** are not formed at this early stage of the electrolysis. Although the material balance of electrolysis products (including unreduced starting material) should be 100%, our analytical data account for only 87% of these species. It is believed that the 'missing product' may be a dimeric dianion **11a**$^{2-}$ (or its protonated form **11a**) which cannot be detected as such: their molecular weight is too high to allow them to be detected by our GC–MS technique; they would be trapped in the injector port of the gas chromatograph.

Scheme 7.

With sulfone **1b**, there is a similar deficiency in the total yield of reduction compounds, although not so large as for **1a**. One must also consider the possibility that coupling of **1·**$^-$ may be a reversible process, which implies that **1·**$^-$ can be reformed fairly rapidly in the bulk solution, especially in increasingly basic solutions as happens at the end of the electrolysis (electricity consumption 1.5 F mol^{-1}). Of course, this cleavage of the C–C bond thereby allows other reactions to occur. In any event, the formation of the dimeric dianion implies the presence of a weak dibasic species in solution, and the base-catalysed isomerization of **1a** to **2a** (or of **1b** to **2b**) should initially be slow (see, for example, Fig. 2b where an almost constant decay of current is seen during the first two minutes of the electrolysis of **1b**, prior to the very steep rise in current that signals the accumulation of **2b**). However, once **2a** (or **2b**) is formed, it can undergo rapid electrolytic cleavage according to a two-

electron process (known behaviour for allyl sulfones), since the allyl sulfone is easier to reduce than the vinyl sulfone. Consequently, as the concentration of the allyl sulfone becomes higher and higher, a self-propagating 'cascade' or 'avalanche' process is established, which accelerates the isomerization (until the supply of **1a** or **1b** is exhausted) (Scheme 8).

Isomerization process. In general, allyl sulfones are thermodynamically more stable than the corresponding vinyl sulfones.[19] Treatment at room temperature of vinyl sulfones **1a** and **1b** with strong bases such as the phosphazene base P$_2$-Et yields equilibrium mixtures with respective allyl:vinyl ratios of 100:0 and 45:55.[7] Such an isomerization process has already been observed during the study of the cathodic behaviour of α,β-unsaturated sulfones of the type ArSO$_2$CH=CHR, where R is an alkyl moiety (C$_2$H$_5$, C$_6$H$_{13}$, or C$_{10}$H$_{21}$).[16]

Inspection of the product distributions obtained in the course of the controlled-potential electrolyses of sulfones **1a** and **1b** (compiled in Tables 2 and 4) clearly indicates that vinyl sulfones **1** isomerize to allyl sulfones **2** throughout the course of electrolysis. This rearrangement is triggered by electrogenerated bases (EGBs). A catalytic process then takes place since, once initiated, the isomerization reaction goes on even in the absence of applied potential.
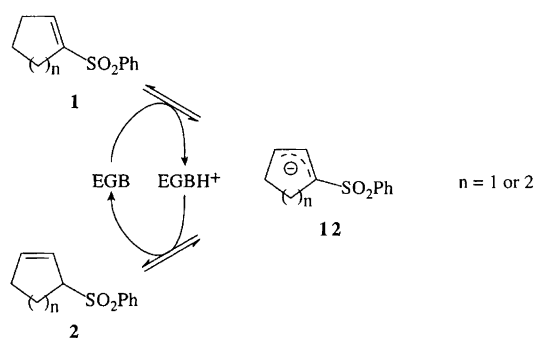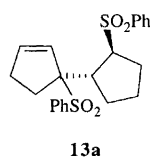

Scheme 9.

The coloration of the solution appearing after a few minutes is attributed to the presence of the delocalized carbanionic species **12**. Moreover, this species should presumably be oxidized at a potential that might correspond to steps C and D as indicated by the increase in the size of the oxidation peaks upon addition of a base. Indeed, the peak potential values for peaks C and D fall within the same range as those previously reported for similar anions.[20]

As shown by the cyclic voltammetry of chemically

Scheme 8.

prepared authentic compounds, allyl sulfones **2** are more easily reducible than the corresponding vinyl sulfones **1** (see Table 1), and are thus responsible for the maximum in the current-time curves of the electrolyses, as well as for the prepeak B observed on the voltammograms of sulfones **1**. The formation of **2b** in a lesser amount than **2a** is in good agreement with the results reported by Fuchs *et al.*[7] Predictably, the cyclic voltammetry of sulfone **1c**, which cannot undergo the isomerization process, does not exhibit any prepeak, and its current-time curve (see Fig. 2) shows normal behaviour (no maximum).

Oligomerization process. The anions of allyl sulfones have proved to be valuable intermediates in Michael additions to activated olefins.[21] On the other hand, vinyl sulfones have been widely used as Michael acceptors not only with 'hard' anions[2] such as organolithium reagents but also with 'soft' ones[2,22,23] such as those derived from nitriles, esters, amides, ketones, or acetylenes. More particularly, 1-cycloalken-1-yl phenyl sulfones **1** have been used in such reactions, and a dimerization corresponding to the conjugate addition of the anion of 1-cyclopenten-1-yl phenyl sulfone **1a** to the vinyl sulfone in the presence of potassium *tert*-butoxide to yield dimer **13a** has been reported.[7]


13a

Scheme 10.

Global yields based on the cycloalkenyl moiety (total 1) obtained during the course of controlled-potential electrolyses of sulfone **1a** reported in Tables 2 and 3 decrease regularly from the very beginning and at the end only 54–58% of the products are accounted for. In addition, this 'disappearance of products' does not require any electricity and appears therefore to be a catalytic process triggered by EGBs. A probable explanation for this phenomenon is the formation of oligomers via Michael addition reactions of anion **11a** as described

below. The oligomers obtained through this process cannot be detected by our GC–MS technique.

For dimeric species **13a** and **15a** obtained by protonation of the corresponding anions, one of the two sulfone groups is of an allylic or vinylic type and consequently should be reduced at the applied potential by analogy with **2a** and **1a**, whereas the other sulfonyl group is an aliphatic one and thus requires a more negative potential to be efficiently cleaved. For oligomers **14a** and **16a**, only one of the $(x+2)$ sulfonyl groups is activated and therefore reducible at the working potential. In the experiment whose results are compiled in Table 3, when the potential is stepped to a more negative value after the electrolysis current decays to the background level, *all* the sulfonyl groups of the oligomers are expected to be reduced. This is indeed what is observed ($n = 1.92$ and total $2 = 96\%$). If 'missing products' were dimers, this should be normally accompanied by a larger amount of detected dimers at the end of the electrolysis. Since this amount does not change significantly, it can be concluded that the oligomerization process does not stop at the stage of the dimers and that higher molecular weight compounds are formed. Preparative-scale electrolyses of **1a** and **1c** have also been performed; they led only, after extraction with ether, to unidentified products whose NMR spectra are compatible with those of oligomers **14** or **16**.

For sulfone **1c** the global yield (total 1) at the end of the electrolysis is much lower (15%) than for sulfone **1a**, implying a much faster oligomerization process which is not unexpected due to the very significant ring strain in this sulfone. On the other hand, the global yield (total 2) in this case is nearly quantitative (97%), in good agreement with the more negative applied potential (-1.60 V) which is sufficient to cleave most of the C–S bonds of the oligomers. What is more surprising is the formation of norbornene (**3c**) when all the starting sulfone has already been consumed (between coulometric *n* values of 0.6 and 1.7). This might be due to a retro-Michael reaction[24] from a dimer or an oligomer (possibly occurring in the GC injector).
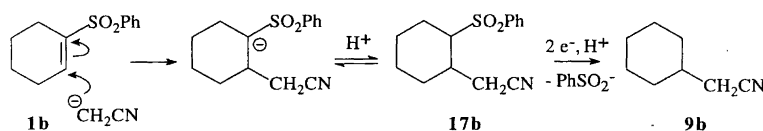
We should stress that dimeric forms **4a** (not electroactive at the electrolysis potential) may be formed in highly
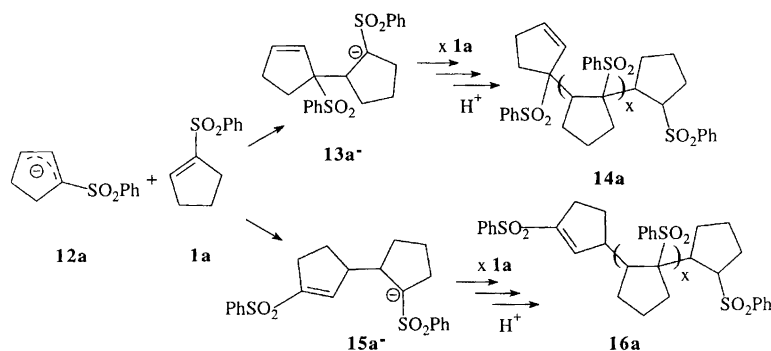
Scheme 11.
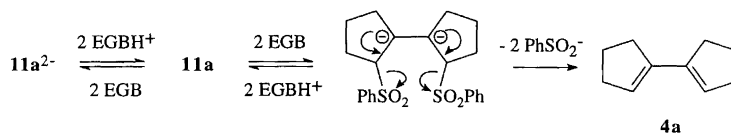
Scheme 12.

Scheme 13.

basic media (end of the electrolysis) by means of a double elimination (Scheme 12).

The intermediate carbanion **13a⁻** (or **15a⁻**) may undergo an elimination process. After isomerization and cleavage, the dimer **4a** would then be obtained. This mechanism is more likely to occur than one in which the dimer **4a** results from a coupling of two cyclopentenyl radicals.

The various carbanions postulated could be responsible for one or both oxidation steps observed in the voltammograms of **1a**. Other experiments involving the addition of proton sources or alkylating agents to the electrolytic medium also favour the oligomerization process and will be reported in future papers.

Reactivity towards acetonitrile. In addition to the products obtained in DMF or in DMSO [cyclohexene (**3b**), dimer **4b**, and dimer **5b**], electrolyses of **1b** in acetonitrile containing 0.1 M TMABF₄ lead to a significant amount (32%) of cyclohexylacetonitrile (**9b**). In relation to the previously mentioned reactivity of 1-cycloalken-1-yl phenyl sulfones **1** as good Michael acceptors, it might be expected that the key step in the formation of **9b** could be the addition of the anion derived from acetonitrile to **1b**. Such deprotonation of acetonitrile by EGBs and addition of the resulting anion to ketones or activated olefins (α,β-unsaturated nitriles) has already been reported.[25] The aliphatic sulfone **17b** obtained after protonation should be reducible at the working potential (−1.65 V) to afford **9b** after electrochemical cleavage (Scheme 13).

Cathodic C–S bond cleavage. The proton source involved in the preparative-scale electrolyses of sulfones **1** should be mainly the supporting electrolyte. Indeed tributyl-amine, arising from a Hofmann degradation of the tetrabutylammonium cation, has been detected in large amount (up to 68% relative to the sulfone) at the end of electrolyses performed in DMF containing TBABF₄ or TBAP.

From a preparative point of view, cleavage selectivity is only observed for the six-membered ring sulfones (90%). With cyclopentene and norbornene derivatives, the ring strain as well as a greater steric access in the

five-membered ring system leads to competing isomerization and oligomerization processes and consequently to much lower alkene yields. It should be pointed out once again that in sulfone electrochemistry an apparently small change in the substrate structure may lead to large discrepancies in cathodic behaviour.

Further experiments involving the addition to the electrolysis medium of proton donors and other electrophiles (such as alkyl halides) have been performed. Results of this work will be described in subsequent papers devoted to the cathodic decomposition of sulfones.

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