

COUPLING BETWEEN RADICAL AND ANION IN THE OUTERSPHERE OXIDATION OF α -SULFONYL CARBANIONS. ITS ROLE ON THE PRODUCT DISTRIBUTION BETWEEN DIMERIC OLEFIN AND DISULFONE

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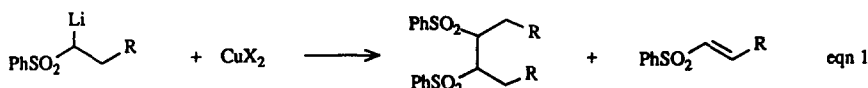
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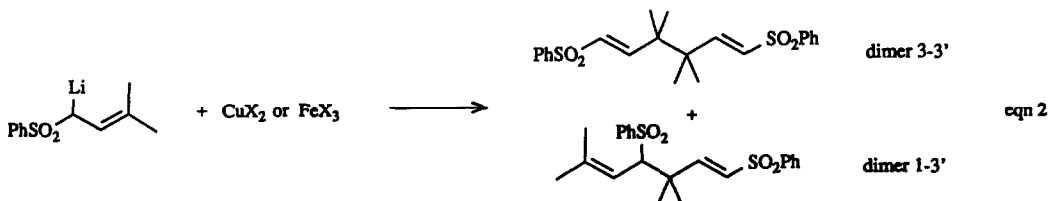
Abstract: The electrochemical oxidation of α -sulfonyl carbanions is shown to involve a coupling reaction between the electrogenerated radical and the parent anionic species, both on preparative and kinetic grounds. Two routes compete for the further evolution of the ensuing anion radical: (i) a two step desulfonylation leading to the dimeric olefin, the product of an overall catalytic process, (ii) or further oxidation leading to the dimeric disulfone. Relevance of this mechanism to transition metal oxidations of α -sulfonyl carbanions is examined.

Introduction.

Transition metal salt oxidation of stabilized carbanions generally leads to the formation of the corresponding dimers¹. In the case of α -sulfonyl carbanions, this reaction is more versatile²⁻⁴ as shown by several studies, namely from Julia's group. Three different products may be obtained depending on the nature and relative amount of the transition metal salt. Reaction of lithiated phenyl alkyl sulfones with a stoichiometric amount of CuX_2 ($\text{X} = \text{Cl}$, acac, CF_3SO_3 , CH_3SO_3 , CF_3CO_2) gives the dimer as the major product, together with the dehydrogenated compound² (eqn.1). However when the counter ion is a carboxylate, the vinylic sulfone is the only product^{2b}.

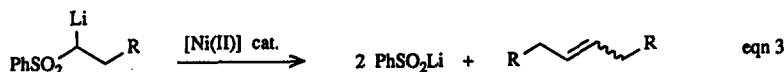


Sulfones with no H atom in the β position (phenyl methyl or phenyl allylic sulfones) yield dimers for all the cupric salts^{2a,3a} as well as with iron(III)^{3b}.



When a catalytic amount of transition metal salt is used -nickel(II) acetylacetonate proved by far the

most efficient catalyst, but the reaction also works with Cu(II) or Fe(III)- the dimeric olefin is formed⁴:



Although no mechanism has been established so far, these reactions are generally thought to proceed by fast transmetallation followed by reactions in the coordination shell of the transition metal salt. This would account for the effect of the salt on the product distribution. However, the different products observed in eqns 1-3 do not correspond to a possible group or atom transfer from the metal complex⁵. Therefore, the specificity of the metal reagent in the above observation can only arise from (i) modification of oxidizing properties by change of the metal or ligands (outersphere effects), (ii) effects due to coordination of intermediates within the metal coordination shell (innersphere effects)⁶.

A direct delineation of the fine interplay between these effects is nearly impossible because one cannot differentiate the closely related outersphere and innersphere properties of the metal catalyst: changing the ligands also leads to a modification of the pure redox properties. By opposition, pure outersphere oxidation, as *e.g.* at an anode, will allow the delineation of effects related to redox properties of the metal center. By comparison to homogeneous situation (see above and eqns 1-3) this will evidence the possible role of innersphere contributions in the case of transition metal oxidants. We have then studied the electrochemical oxidation of α -sulfonyl carbanions.

Electrochemical reduction of sulfones is now a well documented process⁷. By contrast, very little is known about the electrochemical oxidation of their conjugate bases. This may be because these rather basic species (pK_A of sulfones are in the 25 to 29 range in DMSO⁸) are not compatible with common electrochemical media (solvents and supporting electrolytes).

Some polarographic data (half-wave potentials $E_{1/2}$ measured at a rotating disk electrode) have been given for oxidation of such carbanions in DMSO⁹. Also, we briefly described the unexpected cyclodimerisation of phenyl prenyl sulfone anion during preparative scale electrooxidation¹⁰. Finally, the formation of dimers from weakly basic bis or tris α -sulfonyl carbanions has just been reported¹¹.

Results and discussion.

Electrochemical oxidation of phenyl prenyl sulfone carbanion.

Preparative scale electrolysis

The electrochemical oxidation of deprotonated phenyl prenyl sulfone was performed in a divided cell, either in THF (lithium as the counter cation, $n\text{-Bu}_4\text{N BF}_4$ as supporting electrolyte) or in liquid ammonia (potassium as the counter-cation, KBr as the supporting electrolyte). A gold or platinum grid was the anode. The electrolysis consumed about one faraday per mole to go to completion. In both solvents, the major compound formed was a cyclic dimer (C in scheme 1) which has never been obtained by chemical oxidation. Small amounts of the usual dimers 1-3' and 3-3' (see eqn 2) were formed as well as shown in table 1. In the search for an explanation to the formation of this new dimer, we have shown¹⁰ by cyclic voltammetry experiments, that dimer C was generated in high yield from dimer 3-3' by an isomerization process requiring a catalytic amount of monoelectronic reductant. The feasibility of this reaction on a preparative scale was checked by converting the 3-3' dimer into the cyclic dimer C by a slow addition of catalytic amount of

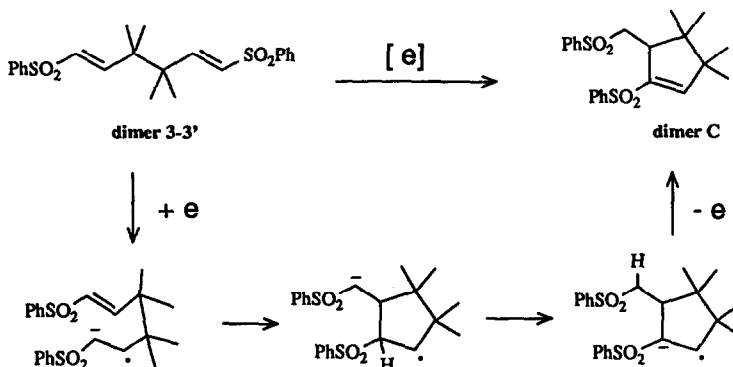
Table 1. Preparative electrooxidation of phenyl prenyl sulfone anion.

Solvent	Recovered prenyl sulfone	dimer 1-3' [*]	dimer 3-3' [*]	dimer C [*]
THF	13%	6% (8)	4% (6)	62% (86)
NH ₃	19%	16% (22)	-	55% (78)

^{*}between parenthesis, ratio of the particular dimer among the three dimers.

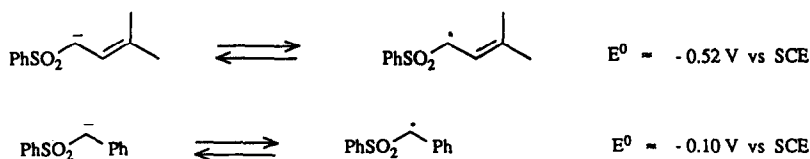
sodium anthracene. The key intermediate of this catalytic process is the anion radical of dimer 3-3' -see scheme 1- which readily undergoes cyclization.

This anion radical must be an intermediate in the prenyl sulfone anion anodic oxidation process as well since it cannot be generated from dimer 3-3' in a medium containing no reducing species (divided cell)¹². This result strongly suggests a coupling reaction between phenyl prenyl sulfone anion and its corresponding radical, the most sensible way to get dimer 3-3' radical anion under oxidative conditions.



Cyclic voltammetry in THF

As shown by high scan rate cyclic voltammetry, monoelectronic oxidation of lithiated phenyl prenyl sulfone gives the corresponding radical, which is very reactive. Indeed, even at 700 V/s, the oxidation wave is only slightly reversible -see fig.1- indicating that the half-life time of the α -sulfonyl radical in the medium (THF, $n\text{-Bu}_4\text{N}^+ \text{BF}_4^-$ 0.3 M, lithiated sulfone 10^{-3}M) is only a few microseconds; A similar result is obtained for phenyl benzyl sulfone anion. It is possible to determine the standard potential for these redox couples which probably constitutes the first thermodynamic data about α -sulfonyl radicals¹³.



At lower scan rates the oxidation wave is chemically irreversible, and remains monoelectronic.

Dependence of the peak oxidation potential on the scan rate was then measured in order to determine whether the fast reaction consuming the intermediate radical was kinetically second order (i.e. radical-radical dimerization) or first order in this transient species¹⁴. Indeed the 27 mV/logv slope found -see fig.2- allowed

Table 2. Peak potentials E^P , and standard potentials E^0 for oxidation of α -sulfonyl carbanions in THF and liq. NH_3 .

	E^P ^{a,b}	E^0 ^b
	-0.13	-0.10
	-0.55 (+0.02)	-0.52
	(+0.44)	(+0.43)
$\text{PhSO}_2\text{CH}_2^-$	(+0.63)	
PhSO_2^-	+0.55 (+1.25)	

^a peak potential were measured at 0.2 Vs^{-1}

^b values in THF (lithium counteraction) in V vs SCE at RT. Values between parenthesis refer to liq. NH_3 (potassium counteraction) in V vs Ag at -38°C .

Figure 1. left: oxidation of lithiated phenyl prenyl sulfone $\approx 10^{-3}\text{M}$ in THF 0.3M $n\text{-Bu}_4\text{NBF}_4$ at 700 Vs^{-1} on a gold disc electrode (ϕ 0.125 mm) at 20°C ; the background subtracted voltammogram is shown on the right hand side.

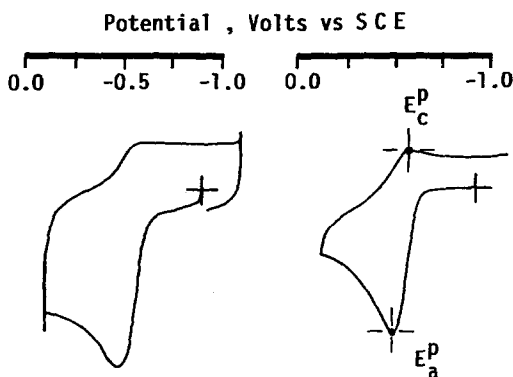
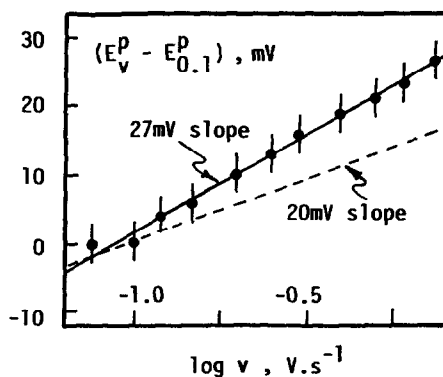


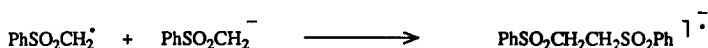
Figure 2. dependence of the oxidation peak potential for lithiated phenyl prenyl sulfone ($\approx 10^{-3}\text{M}$ in THF 0.3M $n\text{-Bu}_4\text{NBF}_4$) on the logarithm of the scan rate; at 20°C gold disc electrode (ϕ 0.5 mm).



Formation of dimer vs formation of olefin during the oxidation of deprotonated phenyl alkyl sulfones.*Electrochemical oxidation of phenyl alkyl sulfone anions.*

While allylic or benzylic carbanions are stable enough in THF $n\text{-Bu}_4\text{N}^+ \text{BF}_4^-$ 0.3 M to allow quick and careful experiments, α -lithiated phenyl alkyl sulfones are very rapidly protonated in this medium so electrochemical experiments are not possible.

However, oxidation of the potassium carbanion of phenyl methyl sulfone can be investigated in liquid ammonia. The oxidation peak potential is shifted about 0.6 V toward positive values from prenyl to methyl carbanion (see table 2), in agreement with a lack of stabilization of the corresponding methyl radical. Peak potential analysis as a function of the potential scan rate once more showed that the radical does not dimerize, since the chemical reaction following the electron transfer is first order with respect to the radical. As no reaction between this radical and the medium (H atom transfer)¹⁷ is possible and no cleavage reaction can take place, we must consider again a coupling with the parent anion as the rate determining step.



No more kinetic information about the fate of the so-formed anion radical of the dimeric disulfone can be obtained from these voltammetry experiments, since the following reactions happen after the rate determining step. However, it is possible to generate this very species independently by mono-electronic reduction of the β -disulfone.

Electrochemical reduction of β -disulfones.

The electrochemical reduction of 7,8-bis benzenesulfonyl tetradecane was then investigated. Preparative scale electrolysis showed that an overall two electron reduction takes place yielding the corresponding olefin tetradec-7ene together with two benzene sulfinate moieties. The electrolysis was performed in acetonitrile with a mercury pool as the cathode; We could show that reduction by homogeneous one electron reducing species (lithium or sodium anthracene) in THF leads to the same result.



This is in full agreement with the reduction of bicyclic β -disulfones by sodium amalgam previously reported¹⁸, and the well known reactivity of sulfones bearing a leaving group in the β position with mono-electronic reducing species¹⁹, including electrodes²⁰.

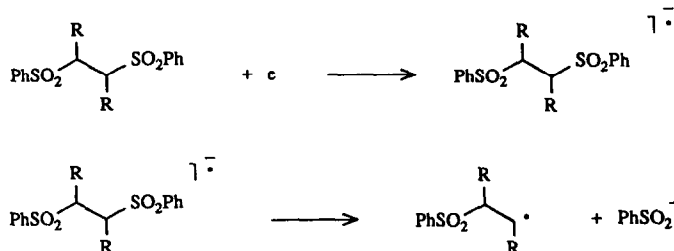
Table 3. Peak potentials E^p for the reduction of phenyl heptyl sulfone and its dimers

7,8-bis benzene sulfonyl tetradecane; at 20°C, vs SCE. potential scan rate: 0.2 V s⁻¹.

Solvent	PhSO ₂ n -C ₇ H ₁₅	meso dimer	d,l dimer
CH ₃ CN	- 2.39 V	-2.14 V	- 2.26 V
THF	- 2.39 V	- 2.11 V	- 2.19 V

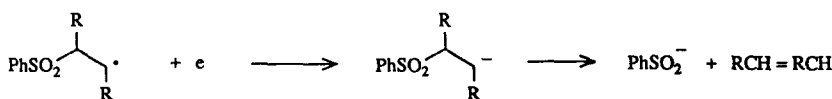
Cyclic voltammetry experiments showed that reduction of the β -disulfone takes place at a less negative potential than reduction of the corresponding monosulfone (phenyl heptyl sulfone). The magnitude of the potential shift depends on the stereochemistry of the dimer, see table 3.

Peak potential analysis of the cathodic wave²¹ showed that the anion radical formed upon electron transfer disappears via a first order reaction; by analogy with reduction of phenyl alkyl sulfones⁷, a fast cleavage of a benzenesulfinate group, yielding a β -sulfonyl radical is the most likely process:

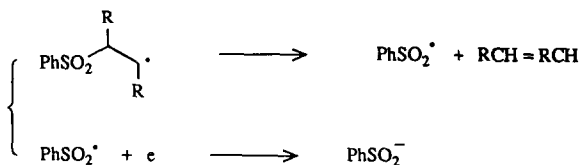


Under strongly reducing conditions, this radical is expected to be reduced to the corresponding anion which would undergo a rapid elimination of the second sulfinate anion. An *a priori* undistinguishable pathway involves β elimination of PhSO_2 from the radical, followed by reduction of the sulfonyl radical.

pathway A:



pathway B:



scheme 2.

Under the large reductive driving force found near the electrode, pathway B may not be able to compete with reduction of the β -sulfonyl radical. However, under non reductive conditions (*vide infra*) this route appears as a likely one for the β -sulfonyl radical evolution²².

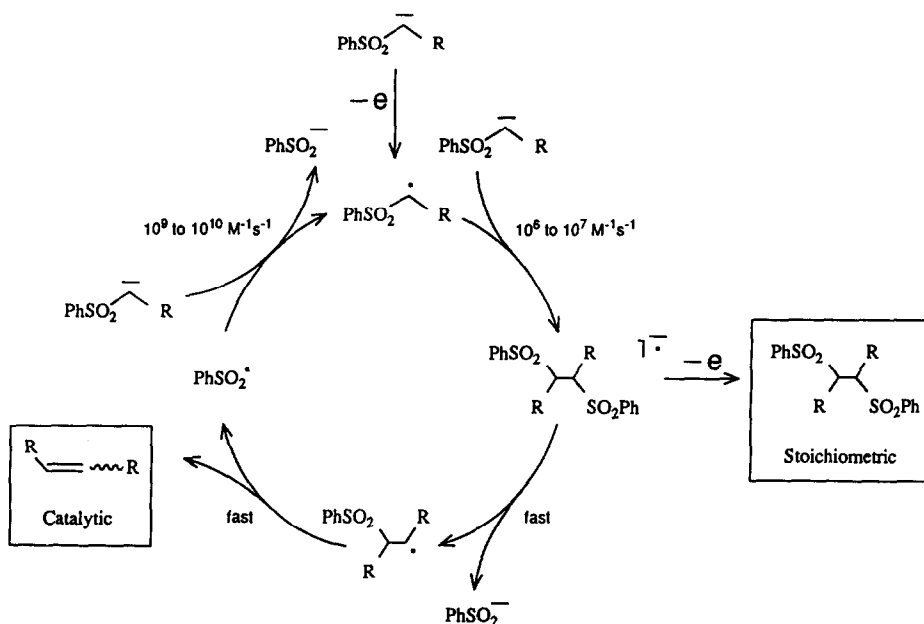
Mechanism of the outer-sphere oxidation of α -sulfonyl carbanions.

From the results given above, it is possible to propose a unifying mechanism for the oxidative coupling of α -sulfonyl carbanions. Mono-electronic oxidation of α -sulfonyl carbanions affords the corresponding radical. This latter undergoes a fast coupling with the parent anion to yield the anion radical of the dimeric disulfone. This key intermediate can either be oxidized to afford the disulfone itself when the experiment is run in the presence of a large amount of oxidant, or undergo a rapid cleavage of a benzenesulfinate anion when the oxidant is present in a catalytic amount. In the latter case, the cleavage will follow pathway B in

scheme 2 since the medium is not reductant^{22b}, and lead to the dimeric olefin together with one sulfinate anion PhSO_2^- and one sulfinate radical $\text{PhSO}_2\cdot$. Oxidation of the α -sulfonyl carbanion (see below and table 2) by $\text{PhSO}_2\cdot$ allows the catalytic cycle to propagate by regeneration of the α -sulfonyl radical. Approximate values^{23a} for the standard free enthalpy of this electron transfer can be determined from the standard potentials in table 2, as shown in table 4. Such values correspond to an electron transfer reaction rate being quite close to the diffusion limit^{23b}.

It appears that the dichotomy between formation of the dimeric olefin and the disulfone reflects the respective contribution of the chain propagation *versus* the termination step.

It has indeed been possible to trigger the catalytic cycle using small amounts of outersphere oxidants^{23b} such as $\text{Fe}(\text{o-phen})_3^{3+}$ or aromatic iodides (2-iodothiophene) and get the alkene (tetradec-7ene) in 20 to 55% yield from lithiated phenyl heptyl sulfone in THF.



scheme 3.

Table 4. Approximate values^{23a} for the standard free enthalpy ΔG^0 of the electron transfer between α -sulfonyl anions and benzenesulfinate radical $\text{PhSO}_2\cdot$: $\Delta G^0 = \mathcal{F}(E^0_{\text{anion}} - E^0_{\text{sulfinate}})$

Anion	$\text{PhSO}_2\text{-CH}^-\text{(Ph)}$	$\text{PhSO}_2\text{-CH}^-\text{(CH}_2\text{=C(CH}_3\text{))}$	$\text{PhSO}_2\text{-CH}^-\text{(C(CH}_3\text{))}_2\text{C(CH}_3\text{)=C(CH}_3\text{))}$	$\text{PhSO}_2\text{CH}_2^-$
ΔG^0 in kJ ^a	- 63	- 103 (- 119)	(- 78)	(- 59)

^a values at 20°C in THF (lithium counteraction); between parenthesis, values at -38°C in liq. NH_3 (potassium counteraction).

The mechanism has been established on the basis of electrochemical data, and involves free radical intermediates and relates to pure outersphere oxidations. As will be discussed later, it should be considered only as a mechanistic frame when transposed to metal salt promoted reactions.

Formation of a "three electron bond".

The key step of these oxidative coupling reactions is the formation of a σ carbon-carbon bond between a radical and a carbanion. Evidence for this is both kinetic (first order in radical) and preparative (cyclisation of the anion radical of the open chain prenyl sulfone dimer). Such a bond formation is not common since it would involve three electrons, one of which located in the σ^* orbital. For this reason, the product is not expected to be stable except if the extra electron can be immediately transferred to another antibonding orbital of much lower energy²⁴. In this case, we assume that this electron is drawn into the π^* orbital of the benzenesulfonyl group, giving a product similar to that of the direct mono-electronic reduction of the disulfone. Consequently, this extra electron is responsible for the cleavage of the carbon sulfur bond which is the second step of the catalytic cycle (scheme 3).

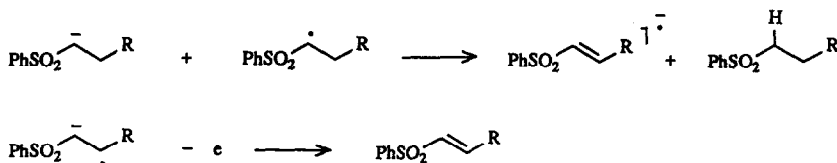
It should be pointed out that such a reactivity is very reminiscent of the oxidation of α -nitro carbanions²⁵ where a radical parent anion coupling process is also involved^{25b}. However, in the latter case, the intermediate anion radical of the dimer is fairly stable: it could be observed by ESR in flow experiments^{25b} and does not cleave before the second oxidation takes place. Such a β -dinitroalkane radical anion has been generated by electrochemical reduction of the β -dinitroalkane and observed by high scan rate cyclic voltammetry²⁶ before it could undergo a cleavage reaction.

Summary and conclusion.

Outersphere oxidation of α -sulfonyl carbanions can lead either to dimeric disulfones (oxidation process) or to dimeric olefins (a process in which the oxidant acts as the initiator of a chain reaction). The orientation toward one product or the other is governed by the chemical evolution of the transient anion radical of the disulfone: further oxidation (chain termination) or cleavage (chain propagation). This mechanistic branching is obviously affected by the amount of oxidant available. This could be the origin of the selectivity of the reaction according to the amount (stoichiometric or catalytic)²⁻⁴ of transition metal oxidant used (compare eqns.1-3). In this respect, innersphere contributions need not to be invoked to rationalize the product distribution.

However, the mechanistic frame in scheme 3 cannot explain the chemoselectivity (dimerization vs dehydrogenation in eqn.1) observed for stoichiometric copper(II) oxidations^{2b}. Indeed, formation of α,β -ethylenic sulfones could be rationalized as in scheme 4²⁷. However the dichotomy between carbon-carbon bond formation vs hydrogen atom transfer in the reaction between one α -sulfonyl radical and the corresponding carbanion has to be related to the specific environment of both species. Therefore, innersphere effects certainly play a significant role on this particular product distribution.

Similarly, such effects have to be responsible for the non formation of the cyclic dimer C in the dimerization of phenyl prenyl sulfone anion by copper(II) or iron(III) compounds. Indeed would a metal free dimer 3-3' anion radical be formed, its cyclization would readily take place.

**scheme 4.****Experimental section.**

All experiments involving α -sulfonyl carbanions were carried out under dry nitrogen or argon using standard Schlenk tube techniques. The ^1H N.M.R. spectra were recorded on a Bruker 250 MHz spectrometer in CDCl_3 with Me_4Si as internal standard, the ^{13}C N.M.R. spectrum was recorded on a Bruker 100 MHz spectrometer, in CDCl_3 ; mass spectra on a Riber R10-10B instrument.

Electrochemical equipment:Electrochemistry in THF.

THF was distilled from benzophenone radical anion, and transferred to a Schlenk tube whose walls were covered with a potassium mirror. Tetrabutyl ammonium tetrafluoroborate was prepared from tetrabutyl ammonium hydrogensulfate and sodium tetrafluoroborate in water, recrystallized from ethyl acetate - petroleum ether, and dried under vacuum (10^{-2} mbar) at 60°C for 6 hours.

Preparative scale electrolyses were performed with a Tacussel PRT 4Q-1X potentiostat which could be connected in series to a power supply, if necessary.

Cyclic voltammetry at the steady disc electrode (gold disc 0.5 or 0.125 mm diameter) was performed with a homemade ultrafast potentiostat with positive feedback ohmic drop compensation^{28a}, and a PAR Model 175 function generator; the voltammograms were recorded with a Nicolet 3091 storage oscilloscope. The auxiliary electrode was a platinum wire.

All the potentials are relative to the saturated calomel electrode (SCE).

Electrochemistry in liquid ammonia.

Ammonia was purchased from Union Carbide, micrographic quality grade, and condensed under inert atmosphere at -60°C just prior to use. The reference electrode was a silver wire pseudo reference, calibrated at the end of each experiment. The auxiliary electrode was a platinum wire.

Preparative scale electrolyses were performed with a Sodilec EDL 20-12 power supply imposing a constant current intensity.

Cyclic voltammetry at the disc electrode (glassy carbon disc 1 mm diameter) was performed with a homemade potentiostat with positive feedback ohmic drop compensation^{28b}, and a Tacussel TPPRT function generator; the voltammograms were recorded with a Nicolet 3091 storage oscilloscope or a Sefram TGM 164 X-Y chart recorder.

Starting sulfones.

The sulfones were prepared as previously described:

phenyl methyl sulfone (methylsulfonyl benzene) m.p. 87°C , lit²⁹. m.p. 88°C ; *phenyl prenyl sulfone (3-methylbut-2-enylsulfonyl benzene)* m.p. 54°C , lit³⁰. m.p. 54°C ; *phenyl benzyl sulfone (phenylmethylsulfonyl benzene)* m.p. 148°C , lit³⁰. m.p. $148-149^\circ\text{C}$.

7,8-bis benzenesulfonyl tetradecane was prepared by copper (II) oxidation of lithiated phenyl heptyl sulfone as reported previously^{2b}.

Preparative scale electrolysisOxidation of metallated phenyl prenyl sulfone.

a) in THF. The divided cell used was connected to the vacuum line. To the anodic compartment containing 70 mL of a 0.3 M solution of $n\text{-Bu}_4\text{N}^+\text{BF}_4^-$ in THF were added, under argon, 5.7 mmol of lithiated phenyl prenyl sulfone dissolved in 10 mL of THF immediately before starting the electrolysis. The working

electrode (anode) was a gold grid, the counter electrode (cathode) a platinum gauze. The potential was imposed vs. a saturated calomel electrode equipped with a bridge containing the same THF/supporting electrolyte solution and separated from the anodic compartment by a glass frit. The electrolysis was set at -0.40 V and after consumption of 500 C (i.e. 90% of one electron per sulfone anion) the current decreased to less than 10% of its initial value. The anolyte was then poured into a saturated aqueous solution of ammonium chloride and extracted three times with dichloromethane. The organic layer was washed with water, dried over magnesium sulfate and evaporated. The crude residue was chromatographed to separate the three dimers.

b) in NH_3 . The divided cell was filled with 120 mL of 0.1 M solution of KBr in liquid ammonia. The auxiliary electrode was a lead rod, the reduction of which leads to anionic amino complexes³¹. The temperature was set at -38°C and 2.5 mmol of phenyl prenyl sulfone were added, followed by 2.5 mmol of potassium tertbutoxide. The constant current intensity was 25 mA, and the disappearance of prenyl sulfone anion was monitored by cyclic voltammetry using a microelectrode (0.5 mm diameter). After 150 C (i.e. 62% of one electron per sulfone anion) the cyclic voltammetry current dropped to zero and the electrolysis was stopped. Addition of 5 mmol of ammonium bromide and slow evaporation under nitrogen of the volatile solvent yielded the crude reaction mixture which was extracted with dichloromethane and chromatographed.

c) description of the products.

1,4-Bis benzenesulfonyl-3,3,6-trimethyl-hepta-1,5 diene E (dimer 1-3'): m.p. 122°C; ¹H N.M.R. 0.90 (br.s, 3H); 1.29 (s, 3H); 1.42 (s, 3H); 1.60 (s, 3H); 3.72 (d, J=12Hz, 1H); 5.26 (d, J=12Hz, 1H); 6.34 (d, J=15Hz, 1H); 7.38 (d, J=15Hz, 1H); 7.45-8.05 (m, 10H). identical to the dimer obtained by chemical oxidation³².

1,6-Bis benzenesulfonyl-3,3,4,4-tetramethyl-hexa-1,5 diene E,E (dimer 3-3'): m.p. 176°C; ¹H N.M.R. 1.03 (s, 9H); 6.22 (d, J=15Hz, 2H); 7.00 (d, J=15Hz, 2H); 7.50-8.05 (m, 10H). identical to the dimer obtained by chemical oxidation³².

1-benzenesulfonyl-5-benzenesulfonylmethyl-3,3,4,4-tetramethyl-cyclopent-1-ene (cyclic dimer): m.p. 123°C; ¹H N.M.R. 0.80 (s,3H); 0.95 (s,3H); 0.99 (s,3H); 1.06 (s,3H); 2.96 (dd, J=8Hz, J=1.7Hz, 1H); 3.41 (dd, J=15Hz, J=8Hz, 1H); 3.99 (dd, J=15Hz, J=1.7Hz, 1H); 6.77 (s,1H); 7.50-8.10 (m, 10H). ¹³C N.M.R. 18.50 (CH₃); 20.79 (CH₃); 25.40 (CH₃); 26.21 (CH₃); 46.98 (C); 47.48 (CH); 48.58 (C); 55.12 (CH₂); 127.71 (2CH); 127.92 (2CH); 129.00 (2CH); 133.39 (CH); 133.58 (CH); 138.54 (C); 139.62 (C); 140.46 (C); 154.40 (CH); MS (E.I. 70eV): *m/z* 419 (M+H), 277 (M-PhSO₂), 197, 135, 125. Anal. Calc. for C₂₂H₂₆O₄S₂: C, 63.16; H, 6.22; found C, 63.15; H, 6.22.

Reduction of 7,8-bis benzenesulfonyl tetradecane.

The cathodic compartment of a divided cell was filled with 100 mL of 0.1 M solution of tetraalkylammonium tetrafluoroborate in acetonitrile; the same solution was used for the anodic compartment and the reference electrode bridge. 480 mg (1 mmol) of the *meso* isomer of 7,8-bis benzenesulfonyl tetradecane^{2b} were then added to the cathodic compartment. The cathode was a mercury pool (7 cm²), the anode a platinum gauze and the reference was a saturated calomel electrode. The electrolysis potential was set at -2.15 V and after consumption of 200 C, the electrolysis was stopped. The reaction mixture was poured into 100 mL of water, extracted three times with pentane. The organic layer was washed with water, dried and evaporated. The yield in tetradec-7-ene was 78% and the isomer ratio E/Z 65/35 (capillary GLC and comparison with authentic sample).

The same procedure from *d,l* isomer^{2b} gave, after electrolysis at -2.35 V, the alkene in a 67% yield and a 85/15 E/Z ratio.

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12.) Another possibility for the formation of cyclic dimer would involve a two electron process induced by addition of a nucleophile on the activated double bond of dimer 3-3'. We could easily show¹⁰ that it was rather unlikely under the electrolysis conditions.

13.) The half-wave potential values $E_{1/2}$ obtained by polarography and reported in ref.9, as well as peak potentials E^p measured by voltammetry are not thermodynamical data since they include kinetic contributions. For a reversible wave, $(E^p - E^0) = (30/n)$ in mV where n, the number of electrons exchanged, is positive for a reduction and negative for an oxidation. However, for a chemically irreversible wave, the peak potential is observed before the above value. see a) Nadjio, L.; Savéant, J.M. *J. Electroanal. Chem.* 1973, 48, 113-145; b) Howell, J.O.; Goncalves, J.M.; Amatore, C.; Klasinc, L.; Wightman, R.M.; Kochi, J.K. *J. Am. Chem. Soc.* 1984, 106, 3968-3976.

14.) When the chemical reaction following the electron transfer ($A - e^-$) is rate determining (*i.e.* the electron transfer step is fast enough) the relationship between the peak potential and the potential scan rate mostly reflects the kinetics of the reaction consuming the transient species T. If this reaction is second order in T (such as a dimerization $T + T$), a 20 mV slope is obtained for the plot of E^p versus $\log v$, for a monoelectronic process at 20°C; the slope is 30 mV for a first order (cleavage, protonation, H abstraction ...) or pseudo first order (coupling of T with its precursor A) reaction. see 13a and Andrieux, C.P.; Savéant, J.M., in Bernasconi, C.F., Ed., *Investigation of Rates and Mechanisms of Reactions*, Vol.6, 4/E, Part 2; J. Wiley and Sons, New-York 1986, Ch.7 pp. 305-390.

15.) In principle, it should also be possible to show, on kinetic grounds, that the first order reaction actually is the coupling with the parent anion A: in such a case, the peak potential depends on the concentration in A (with a theoretical slope of 30 mV per unit of $\log c$), whereas no dependence is to be found for a monomolecular reaction involving T only; see 14. In our case, reliable measurements of E^p at very different concentrations were difficult because of the unstability of the anion in the medium; however an intermediate value of 12 to 15 mV for this slope was generally obtained which means that two reactions compete to consume the α -sulfonyl radical: the coupling with the anion and another reaction, likely to be H atom transfer from the medium (THF and tetraalkyl ammonium cations).

16.) The theoretical values of 20, and 30 mV per logarithm unit at 20°C for the slopes¹⁴ become respectively 15 and 23 mV at -38°C. The experimental value for oxidation of prenyl sulfone carbanion in liquid ammonia was 20 mV.

17.) Amatore, C.; Pinson, J.; Savéant, J.M.; Thiébaud, A. *J. Am. Chem. Soc.* 1982, 104, 817-826 and ref. therein.

18.a) De Lucchi, O.; Modena, G. *J. Chem. Soc. Chem. Comm.* 1982, 914-915; b) De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* 1984, 49, 596-604.

19.) See Julia, M.; Paris, J.M. *Tetrahedron Lett.* 1973, 4833-4836 for the first reported example.

20.a) See ref.5, p.1036 and Gambino, S.; b) Martigny, P., Mousset, G.; Simonet, J. *J. Electroanal. Chem.* 1978, 90, 105-116; c) Berdnikov, E.A.; Federov, S.B.; Kargin, Yu.M. *Zh. Obshch. Khim.* 1978, 48, 875-878.

21.) A slope of 30 mV per decimal logarithm unit is determined for reduction of the meso^{2b} isomer of 7,8-bis benzenesulfonyl tetradecane in acetonitrile. In the case of the other diastereoisomer, the electron transfer is slow^{13a,14}, so no reaction order could be obtained on the fate of the anion radical. A slow electron transfer means that a significant internal rearrangement is associated with this electron transfer. Such a different behaviour seems to imply that the second benzenesulfonyl group participates in the electron transfer to the first one (different E_p).

22.a) For the cleavage of PhSO_2 from a β -sulfonyl radical, see Boothe, T.E.; Greene, J.L.; Shevlin, P.B. *J. Org. Chem.*, 45, 794-797. b) If this latter cleavage is not fast enough, a third route can be considered which involves reduction of the β -sulfonyl radical by the α -sulfonyl anion itself. The validity of this route could not be established since reduction of β -sulfonyl radicals could never be observed by cyclic voltammetry.

23.a) For the values in table 4, standard potentials E^0 were used except when these were not available, *i.e.* for PhSO_2^- and $\text{PhSO}_2\text{CH}_2^-$. For these latter, peak potentials at 0.2 V/s were used instead (table 2) which introduces a systematic error¹³. Therefore, the real ΔG^0 values are expected to be more negative than those given in table 4 except may be for the case of $\text{PhSO}_2\text{CH}_2^-$ oxidation by PhSO_2^- . In this case, a maximum error of ca. 15 kJ/mol is expected. b) As soon as $\Delta G^0 < -25$ kJ/mol, the rate of electron transfer is controlled by the diffusion limit: see Schlesener, C.J.; Amatore, C.; Kochi, J.K. *J. Am. Chem. Soc.* 1984, 106, 3567-3577.

24.) see *e.g.*: Rossi, R.A.; Rossi, R.H. in *Aromatic Substitution by the $\text{S}_{\text{RN}}1$ Mechanism*, ACS Monograph 178, Washington DC 1983, Ch.6 pp.143-160 and ref. therein.

25. a) Shechter, H.; Kaplan, R.B. *J. Am. Chem. Soc.* **1953**, *75*, 3980-3983; b) Edge, D.E.; Norman, R.O.C.; Storey, P.M. *J. Chem. Soc. (B)* **1970**, 1096-1099.

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27. a) α -Sulfonyl radicals readily abstract *hydrogen atoms* from good donors, see Julia, M., Rolando, C., Verpeaux, J.N. *Tetrahedron Lett.* **1982**, *23*, 4319-4320. The α -sulfonyl anion may be a good H donor since such a transfer would leave the rather stable⁷ vinylic sulfone anion radical; for an analogy with H atom transfer from alcoholates, see Amatore, C.; Badoz-Lambling, J.; Bonnel-Huyghes, C.; Pinson, J.; Savéant, J.M.; Thiébaud, A. *J. Am. Chem. Soc.*, **1982**, *104*, 1979-1986. b) The same vinyl sulfone anion radical may also be formed by a *proton* transfer from the α -sulfonyl radical. In term of enthalpy, this reaction is identical to the above one and is therefore favorable on thermodynamic grounds. Compare the enhanced acidity of hydroxyradicals vs. alcohols: see Bunnett, J.F.; Wamser, C.C. *J. Am. Chem. Soc.*, **1967**, *89*, 6712-6718 and refs. therein.

28.a) Amatore, C.; Lefrou, C.; Pflüger, F. *J. Electroanal. Chem.* **1989**, *270*, 43-59; b) Garreau, D.; Savéant, J.M. *J. Electroanal. Chem.* **1972**, *35*, 309-331.

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30.) Julia, M.; Uguen, D. *Bull. Soc. Chim. Fr.* **1976**, 513-518.

31.) Acidic and Basic Solvents, in Lagowski, J.J., Ed., *The Chemistry of Non-aqueous Solvents*, Academic Press, New-York 1967, Vol.II, Ch.7 p.347.

32.) see refs. 2a, 27a and 3b for preparation of authentic samples and Rolando, C. *thesis* University of Paris, France, 1984 for previous descriptions of pertinent spectra.